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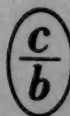
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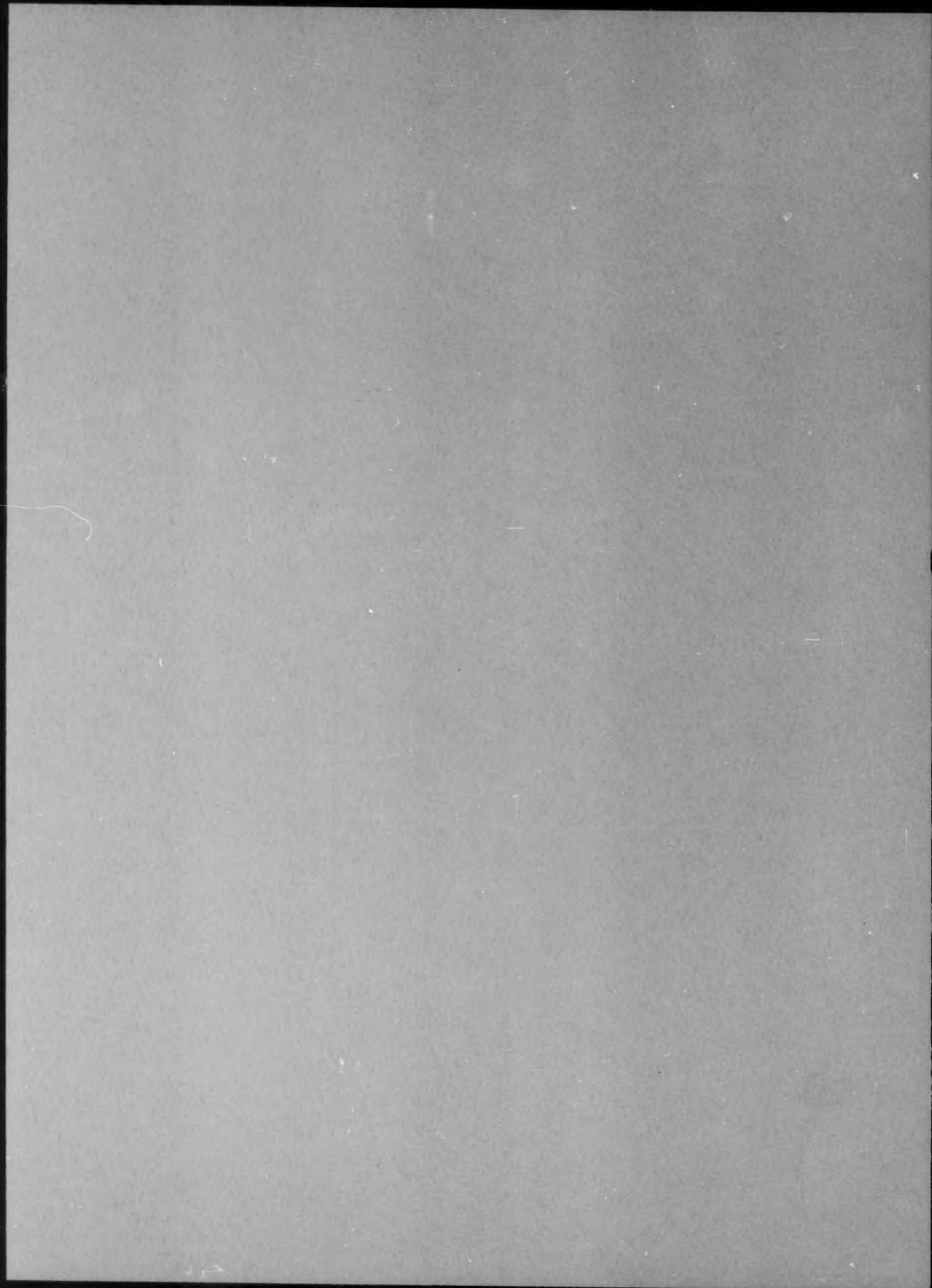
Chemistry Section

ДОКЛАДЫ АКАДЕМИИ НАУК СССР
(DOKLADY AKADEMII NAUK SSSR)

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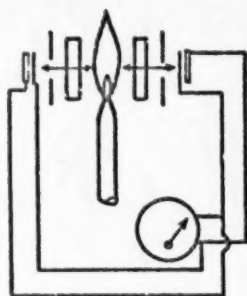
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Chemistry Section

IN ENGLISH TRANSLATION



CONSULTANTS BUREAU



TECHNIQUES IN FLAME PHOTOMETRIC ANALYSIS

by N. S. Poluéktov

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This volume contains a practical and comprehensive survey of the techniques employed and the instruments required for this important rapid analysis method, as well as a brief account of the theoretical principles involved. Experimental procedures and the design of apparatus are discussed at length, making the relevant chapters a valuable manual for all chemists concerned with analytical problems.

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TRIETHYL LEAD OXIDE

Yu. A. Aleksandrov, T. G. Brilkina, and V. A. Shushunov

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(Presented by Academician M. I. Kabachnik, July 4, 1960)

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Triethyl lead oxide $[(C_2H_5)_3Pb]_2O$ can be formed as an intermediate product in the oxidation of hexaethyl dilead by oxygen. As was observed earlier [1], the reaction of hexaethyl dilead with oxygen has a clear induction period. If a solution of hexaethyl dilead is previously treated with triethyl lead oxide, the induction period in this reaction is greatly shortened, nearly to complete disappearance.

In Fig. 1 we present graphically the experiments on oxidation of hexaethyl dilead by oxygen at a pressure of 300 mm Hg in a solution of n-nonane at 60°. Curve 1 shows absorption of oxygen by the solution of hexaethyl dilead with time of the reaction. Curve 2 shows this process under the same conditions when, before oxidation of the hexaethyl dilead, about 1.3 mole % of triethyl lead oxide was added to the solution. The hastening of the reaction observed here is explained by the fact that triethyl lead oxide splits with formation of free radicals, which depends on degeneration of a branching chain.

For a more detailed investigation of triethyl lead oxide we synthesized it and studied some of its properties.

Although triethyl lead oxide was known from the work of Löwig [2] and Klippel [3], carried out more than a hundred years ago, and also from the recently published work of Gilman and co-workers [4], actually this compound was not obtained by them. In the course of carrying out the synthesis these investigators used alcoholic and water solutions in which, as will be shown below, triethyl lead oxide is easily hydrolyzed.

Oxides of other triethyl lead compounds also have not been synthesized.

Our synthesis of triethyl lead oxide is based on the reaction of triethyl lead monohydroxide with metallic sodium, carried out at room temperature under a layer of dry benzene. To carry out this reaction metallic sodium was first dispersed in n-nonane and then separated from the hydrocarbon, first by decantation of the liquid and then by distillation of the residue at room temperature and reduced pressure (about 0.2-0.5 mm Hg), after which the metal was put under dry benzene. An amount of triethyl lead monohydroxide was added to this heterogeneous mixture in such quantity that the metallic sodium was in considerable excess.

In the course of the reaction the triethyl lead monohydroxide, comparatively insoluble in benzene at room temperature, was converted to the easily soluble triethyl lead oxide. After 2-3 hr, when the reaction had almost ended, the solid component of the reaction mixture was separated from the solution by filtration, and the benzene was distilled off at room temperature and reduced pressure. After this distillation there remained in the flask a mobile, weakly yellow-green liquid which had a sharply characteristic odor, and a small amount of triethyl lead monohydroxide which crystallized out when the benzene was distilled. This mixture was filtered once more through a thick glass filter.

Study of the composition and properties of the filtrate showed that this substance was triethyl lead oxide. The results of its analysis: found lead content 68.2 and 68.9% (calculated 68.5%); molecular weight determined by lowering of freezing point of benzene, 590, 592, 588 (calculated 604).

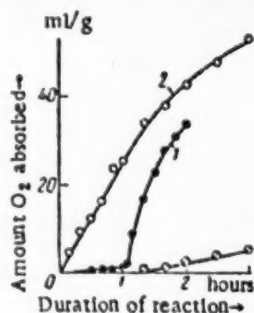


Fig. 1. Oxidation of hexaethyl dilead by oxygen. Initial concentration of hexaethyl dilead 20 mole %.

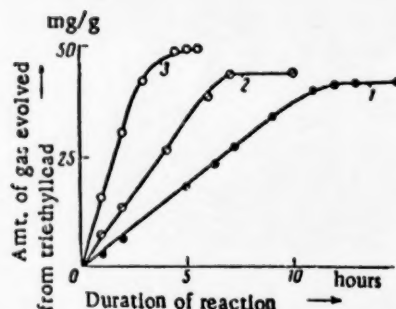
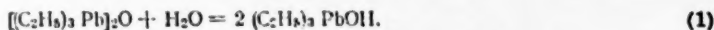


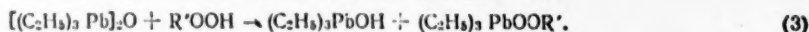
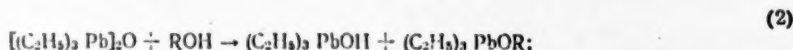
Fig. 2. Decomposition of triethyl lead oxide at different temperatures. Curves 1, 2, and 3 were obtained at 70, 80, and 90°.

Triethyl lead oxide even at room temperature was very easily hydrolyzed to triethyl lead monohydroxide:



In the hydrolysis product we found by titration with hydrochloric acid 98-99% triethyl lead monohydroxide.

Alcohols act on triethyl lead oxide in an analogous manner, and also tertiary alkyl and arylalkyl hydroperoxides, which give oxide and peroxide compounds of triethyl lead, and also triethyl lead monohydroxide.



Both these reactions take place with great speed even at 10° below zero. The resulting oxides and peroxides are very easily hydrolyzed, and at higher temperatures are decomposed. For this reason, reactions (2) and (3) were run at low temperature (gradually rising from -10° to 0°) and at low initial concentrations (about 0.2 mole/liter) of reacting substances in hexane solution. The experiments were carried out in an apparatus which permitted exclusion of air from the reaction mixture. The combination of these precautionary measures in running reactions (2) and (3) prevented hydrolysis of the oxides and peroxides by water vapor from the air, and also their oxidation and thermal decomposition.

We studied the reaction of triethyl lead oxide with methyl, ethyl, and benzyl alcohols, with dimethylphenyl carbinol, and also with tert-butyl hydroperoxide and with α -cumyl hydroperoxide.

As was recently established [5], at room temperature triethyl lead monohydroxide hardly reacts at all in aliphatic hydrocarbons. This permitted us to separate the precipitates formed in reactions (2) and (3) by filtration from the solution of the other organic lead compounds and to characterize them qualitatively and quantitatively. In all our experiments carried out for this purpose, the results showed that the precipitate was triethyl lead monohydroxide in amounts which as a rule were 95-100% of the theory.

In the experiments on studying the reaction of triethyl lead oxide with ethyl alcohol, with tert-butyl hydroperoxide, and also with α -cumyl hydroperoxide we isolated and characterized the products of reactions (2) and (3), which were formed along with triethyl lead monohydroxide. For this purpose, 5-7 min after mixing solutions of the starting substances in n-hexane with the precautions mentioned above, we filtered the precipitate from the reaction mixture through a thick glass filter. Then at about 0° and reduced pressure the volatile compounds were distilled from the filtrate. The remaining substance was characterized by its content of lead and hydroxyl groups which were formed after it was treated with water, and also by its molecular weight, determined by lowering the freezing point of benzene. The results of these determinations are given in the table.

Compound formed	Molecular weight		Found, of amount calculated by theory, %	
	calcd.	found	lead	hydroxyl groups after hydrolysis
$(C_2H_5)_3PbOC_2H_5$	339	324; 344	92	94; 99
$(C_2H_5)_3PbO_2C(CH_3)_3$	383	374	—	100
$(C_2H_5)_3PbO_2C(CH_3)_2C_6H_5$	445	415	99; 101	99

As the table shows, in our experiments we actually obtained ethoxytriethyl lead, tert-butylperoxytriethyl lead, and α -cumylperoxytriethyl lead, and also some other analogous compounds.

The experiments carried out for quantitative determinations showed that per mole of triethyl lead oxide which reacted with one mole of alcohol or hydroperoxide there was formed 0.9-1.0 mole of triethyl lead monohydroxide and 0.9-1.0 mole of the corresponding oxy or peroxy lead organic compound.

Freshly prepared ethoxytriethyl lead $(C_2H_5)_3PbOC_2H_5$ was a colorless, crystalline substance melting at about 20° and fuming in air. This agreed with the results of Gilman and Abbat, given in a review [6]. Methoxytriethyl lead $(C_2H_5)_3PbOCH_3$ was a cream-colored crystalline substance which decomposed without melting when heated to $60-70^\circ$. α -Cumyloxytriethyl lead $(C_2H_5)_3PbOC(CH_3)_2C_6H_5$ was slightly mobile at room temperature and had a weak yellow-green color. Tert-butylperoxytriethyl lead $(C_2H_5)_3PbO_2C(CH_3)_3$ and α -cumylperoxytriethyl lead $(C_2H_5)_3PbO_2C(CH_3)_2C_6H_5$ were viscous pale golden liquids.

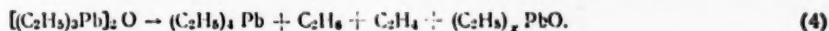
All of our oxy and peroxy compounds were unstable and in a sealed ampoule even at room temperature slowly decomposed, acquiring a red-brown color which strengthened with time.

Triethyl lead oxide at room temperature reacted very energetically with acetone. Thus, on running this reaction in dilute hexane solution with equimolecular ratio of triethyl lead oxide and acetone, there was immediate separation of a colorless crystalline precipitate, which by its content of lead and hydroxyl groups was identified as triethyl lead monohydroxide.

When triethyl lead oxide was mixed with a great excess of acetone we also found formation of a colorless crystalline product. The solution above the precipitate at room temperature gradually became dark brown. As a reaction product we showed the formation of mesitylene oxide, which was isolated as a fraction in distillation of the reaction mixture and by reaction with 2,4-dinitrophenylhydrazine; there was also a small amount of intensely dark brown, tarry, higher boiling products, which we did not study further. The reaction of triethyl lead oxide with acetaldehyde took place in an analogous manner. In this case the reaction mixture above the precipitate gradually changed from a mobile and colorless liquid to a viscous, pale yellow mass.

Triethyl lead oxide decomposed slowly at room temperature and much faster when heated, forming gaseous, liquid, and solid products. Figure 2 shows three kinetic curves which show how the evolution of gas occurs with time for this reaction at different temperatures. We showed by the chromatographic method that the gas thus evolved consisted of an equimolecular mixture of ethane and ethylene with about 1% by volume of butane. The reaction products remaining after removal of the gas consisted of a mixture of a clear liquid and a cream-colored precipitate. This liquid was distilled from the precipitate at reduced pressure and identified by reaction with monochloroacetic acid as tetraethyl lead [7], whose yield reached 0.97 mole per mole of decomposed triethyl lead oxide. We did not investigate the solid product in detail, but showed that it contained lead (87.5%), an organic residue (probably the ethyl radical) and was almost insoluble in the usual organic solvents.

The thermal decomposition of triethyl lead oxide can be represented by the following reaction scheme:



The formation of ethane and ethylene in this reaction can be explained by the disproportionation of the ethyl radical, whose presence, in our opinion, is the reason for the above observed hastening effect of the triethyl lead oxide addition on the oxidation of hexaethyl dilead by oxygen. If water was first added to the hexaethyl dilead solution and the oxidation by oxygen carried out, then the intermediate product here formed, the triethyl

lead oxide, would be at once hydrolyzed to triethyl lead monohydroxide, and the oxidation reaction would proceed very slowly. Curve 3 (Fig. 1) shows how the absorption of oxygen occurs in the oxidation of hexaethyl dilead in the presence of added water.

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A STUDY OF THE EXCHANGE OF ETHYL RADICALS
IN THE SYSTEM $\text{Al}(\text{C}_2\text{H}_5)_3 - \text{C}_2\text{H}_5\text{Br}$

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(Presented by Academician M. I. Kabachnik, July 11, 1960)

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In previous work we studied the possibility and conditions for the exchange of radicals in some organic derivatives of mercury [1], lead [2], and magnesium [3]. Considering the increasing interest in organic aluminum compounds, which are widely used in organic syntheses, we have studied the exchange of the ethyl radical between triethyl aluminum and ethyl bromide. We should remark that the study of the exchange of the same alkyl or aryl radical is possible only by the method of radioactive indicators. Therefore one of the components of the system under study, namely ethyl bromide, was labeled with C^{14} . The synthesis of labeled ethyl bromide was carried out by the method described earlier [2].

In connection with the high sensitivity of triethyl aluminum to moisture and oxygen, all the work of filling the reaction ampule with the starting components was carried out in an atmosphere of purified nitrogen. The filled ampule was frozen with liquid nitrogen, evacuated, sealed and placed in a thermostat under the desired conditions. If exchange of radicals occurs in the system studied, then the ethane collected from the decomposition of triethyl aluminum after running the exchange reaction should contain C^{14} . Radiometric analysis of the ethane for its C^{14} content was carried out on an internally filled counter after first burning the ethane to carbon dioxide [4].

The generalized data obtained in the study of exchange of ethyl radicals in the system triethyl aluminum-ethyl bromide show the following characteristics: a) The necessary conditions for radical exchange in this system are the presence of metallic halides, without the addition of which exchange does not occur even under rather severe conditions (150°, 20 hr); b) in the presence of TiCl_4 and NiCl_2 there is either an explosion of the ampule or polymerization of the starting substances, as a result of which there is formed a thick, tarry mass which is not decomposed by alcohol or water; c) in the presence of EtCl_3 , FeCl_3 , CuCl_2 , CuCl , CoCl_2 , AgBr , and SnCl_2 the exchange reaction occurs smoothly, as a rule without explosion; d) gases are not formed as side products of the reaction; e) the exchange reaction is monomolecular (the rate constants for the exchange reaction are calculated by the equation:

$$K = -\frac{1}{t} \ln \left(1 - \frac{A_t}{A_\infty} \right),$$

where t is time in seconds, A_t the activity of triethyl aluminum at time t , A_∞ the activity of triethyl aluminum at equilibrium, that is, at 100% exchange); f) in diethyl ether as the solvent the rate of exchange falls sharply.

The experimental data are given in the table.

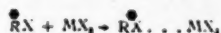
On the basis of the above characteristics we assume that the exchange reaction occurs through formation of a six-membered cyclic complex with alternate rupture and formation of bonds [5, 6]. As additives we used

Additive	Sol-vent	Temp. K. $\cdot 10^{-5}$, °C	sec ⁻¹	E, kcal/mole	Additive	Sol-vent	Temp. K. $\cdot 10^{-5}$, °C	sec ⁻¹	E, kcal/mole
BiCl ₃	—	90	6.13	10.5	CuCl	—	85	4.33	6.5
	—	100	8.82			—	100	6.23	
	—	115	15.54			—	115	8.82	
	Ether	100	0.052	9.0	CoCl ₂	—	85	1.92	9.0
		115	0.072			—	100	3.36	
120		0.096	—			115	5.09		
FeCl ₃	—	85	3.37	8.0	AgBr	—	100	0.50	11.0
	—	100	6.13			—	115	0.96	
	—	115	8.18			—	135	1.82	
	Ether	100	0.041	13.0	SnCl ₂	—	100	0.38	6.0
		110	0.052			—	115	0.53	
125		0.086	—			135	0.77		
CuCl ₂	—	85	4.13	7.0					
	—	100	6.80						
	—	115	9.34						

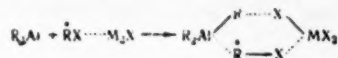
metal halides which had d-electrons in their orbits. For elements with d-electrons it is characteristic to have close s-, p-, and d-levels, due to which there is possibility of reciprocal transfer between them with increased number of single electrons. The unpairing of electrons leads to increased valence, as a result of which there can occur additional bonds over the ordinary valence, which can cause, it would seem, reactions of "saturated" molecules with each other.

In our opinion the exchange reaction includes three stages:

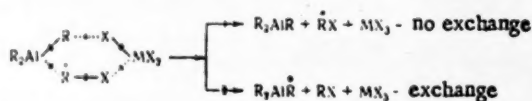
1) The alkyl halide and the metal halide form a polarized molecular compound in which, because of the polarization there is loosening of the covalent bond carbon-halogen



2) Triethyl aluminum and the polarized molecular compound form a six-membered cyclic complex



3) The six-membered cyclic complex splits either with rupture of the formed bonds (dotted lines, once struck across), or with rupture of the old loosened bonds (solid line, twice struck across).



The stage of splitting of the cyclic complex, which can be considered a pseudomolecule, is a monomolecular reaction. The reaction scheme does not assume formation of a gas as a by-product of the exchange reaction.

The presence of an empty orbit in the aluminum atom in triethyl aluminum facilitates formation of the cyclic complex. It would naturally be assumed that if the empty orbit of the aluminum atom were occupied, it would be difficult to form the cyclic complex, and hence the exchange of radicals would be difficult. It is known that triethyl aluminum forms an etherate with diethyl ether which is a very stable compound. Therefore we studied the exchange in our system in a diethyl ether medium, where the empty orbit of the aluminum atom is occupied by formation of a donor-acceptor bond between aluminum and the oxygen of the ether. In this case, the exchange decreases (table).

Thus, the above characteristics of the reaction agree well with the assumed mechanism of the exchange.

The authors are very grateful to Corresponding Member, Academy of Sciences, USSR G. A. Razuvaev for discussion of this work.

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DERIVATIVES OF SILANES WITH HYDROCARBON BRIDGES BETWEEN THE SILICON ATOMS

POLYMERIZATION OF 1,1-DIMETHYLSILICACYCLOPENTANE

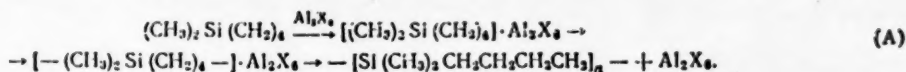
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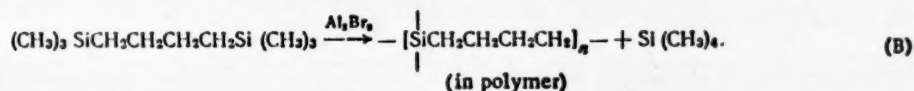
Original article submitted October 1, 1960

In the work of three of us [1, 2] we described a reaction, specific for the chemistry of organosilicon compounds, for polycondensation of disilanes with hydrocarbon bridges between the silicon atoms; reaction takes place under the influence of aluminum halides. Thus, in the case of compounds of the type $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_k\text{Si}(\text{CH}_3)_2$, where $k = 1, 2, 3, 6$, reaction occurs with formation of tetramethylsilane and polymeric silicohydrocarbons which consist of repeated groupings $\text{Si}(\text{CH}_2)_k\text{Si}$, and depending on conditions of reaction and the value of k there are obtained cyclic polymers (of the type $[\text{Si}(\text{CH}_2)_k\text{Si}]_n$), linear polymers (of the type $\text{CH}_3[\text{Si}(\text{CH}_2)_k\text{Si}]_n\text{Si}(\text{CH}_3)_2$), or trimers. These reactions are evidently general for compounds of the $(\text{CH}_3)_2\text{Si}-\text{R}-\text{Si}(\text{CH}_3)_2$ type; we have established in particular that when R is arylene, under the influence of aluminum halides there also occurs a reaction of condensation of these silicohydrocarbons. The reason for such a course of the reaction, in our opinion, is the unequal stabilities of the bonds $\text{Si}-\text{CH}_3$ and $\text{Si}-\text{R}$ (less in the latter case) under the action of the aluminum halide.

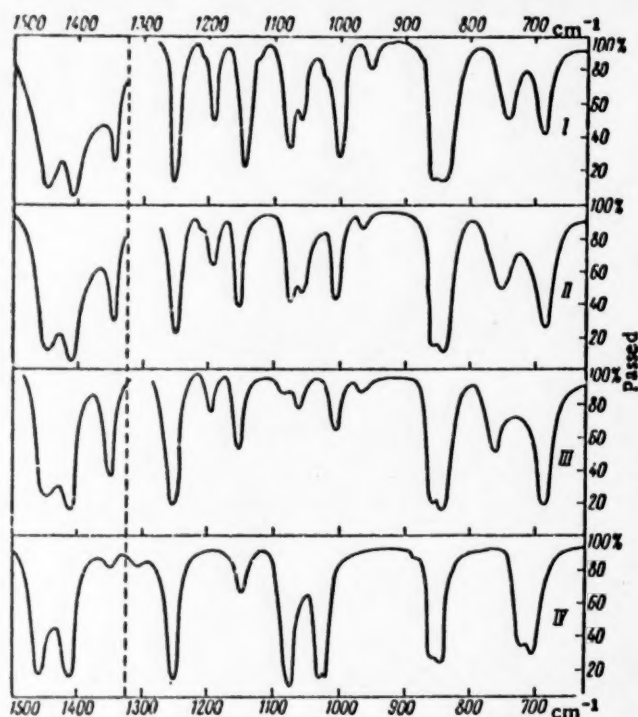
In the present work we have studied the action of aluminum halides on 1,1-dimethylsilicacyclopentane. Considering this silicohydrocarbon as a characteristic bridge compound in which the radical R is bound to one and the same silicon atom, we have assumed that here also $\text{Si}-(\text{CH}_2)_4$ will be more active under the influence of AlX_3 than the bond $\text{Si}-\text{CH}_3$. In this case we can expect formation of a reactive radical $-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. The experimental data confirm this assumption. It was shown that in the presence of AlCl_3 and AlBr_3 there is a specific polymerization reaction, which can be represented by scheme (A):



Transformation occurs very energetically after short heating of the silane with the catalyst.* To show the structure of the resulting product we carried out the countersynthesis of the polymer composed of analogous fragments by scheme (B):



*In contradiction to this, in reaction of 1,1-dimethylsilicacyclopentane with concentrated H_2SO_4 , as was shown earlier [3], there is quantitative rupture of the bond $\text{Si}-\text{CH}_3$, and the bond $\text{Si}-(\text{CH}_2)_4$ in the ring is not touched.



Infrared spectra of starting and polymeric compounds. I) Polymer of 1,1-dimethylsilicacyclopentane; II) polymer of 1,4-hexamethyldisilylbutane; III) 1,4-hexamethyldisilylbutane; IV) 1,1-dimethylsilicacyclopentane.

The infrared spectra of the polymers* (see figure) prepared by scheme (A) (spectrum I) and (B) (spectrum II) were identical, which gives a basis for assuming the identity of the structural elementary chains which form these polymers. Judging by the spectrum of 1,4-hexamethyldisilylbutane (spectrum III) the structure of the elementary unit of the polymer is the same as in this monomeric compound; in spectra I and II there are present bands 740, 1005, 1060, 1075, and 1195 cm^{-1} , which are characteristic of III. At the same time, the spectrum of 1,1-dimethylsilicacyclopentane (IV) differs markedly from spectrum I.

It can be seen that in the region of valence oscillation of the C—C bond in the spectrum of monomer III and polymers I and II there are bands at 1060 and 1075 cm^{-1} with different relative distributions of intensity in each of these spectra. It is possible that this difference can be explained by spatial arrangement (repeated isomerism) of the chain C—C—C in the monomer and polymers.

Starting substances. The syntheses of 1,1-dimethylsilicacyclopentane and 1,4-hexamethyldisilylbutane were carried out by the methods described in [4, 5], starting from 1,4-dibromobutane. 1,4-Hexamethyldisilylbutane was obtained as follows. To 60 g of $(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ [6] and 2 drops of 0.1 N solution of H_2PtCl_6 in isopropyl alcohol was slowly added 40 g of methyldichlorosilane in a boiling mixture. When the temperature of the mixture reached 125°, we added 14 g more of methyldichlorosilane and then boiled the mixture for four hr. By distillation we obtained 65.5 g (63% of theoretical) of 1-trimethylsilyl-4-methyldichlorosilylbutane, b. p. 220–223°, n_D^{20} 1.4445; d_4^{20} 0.9625. M_R found 67.2, calculated 67.0. Found %: Cl 29.4, 29.5. Calculated for $\text{Si}_2\text{C}_8\text{H}_{20}\text{Cl}_2$ 29.2%.

By reaction of methylmagnesium chloride (from 30 g Mg) and 82 g of $(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiCl}_2\text{CH}_3$ in 800 ml of absolute ether we obtained 1,4-hexamethyldisilylbutane with b. p. 193–200°. By distillation of the crude product on a column with 20 theoretical plates we obtained 80 g (95% of theoretical) of disilylbutane with b. p. 196–197° (atm), n_D^{20} 1.4270, d_4^{20} 0.7655. The properties and spectrum of the preparation obtained by this method and the method of [5] were identical.

* The infrared spectra were photographed on an IKS-12 apparatus in the region 700–1300 cm^{-1} in a thin layer between glass and in the region 1300–1500 cm^{-1} in a layer 0.1 mm thick; NaCl prism.

Polymerization of 1,1-dimethylsilacyclopentane. We heated 5.16 g of $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_4$ and 0.34 g (2.6 mole %) AlBr_3 for 2 min at 120-130° in a flask with a reflux condenser, with energetic stirring of the mixture by a magnetic stirrer. Thus without boiling, the contents of the flask were converted into a light yellow, clear, and very viscous mass. The weight of the reaction mixture after polymerization was 5.47 g. The polymer was dissolved in 50 ml of ether; the ether solution was washed several times with distilled water and dried over CaCl_2 . After distillation of the ether and vacuum treatment of the residue at 70-80°/3 mm for an hour, we obtained a polymer (4.1 g, 80% of theoretical) which was very viscous, almost glassy, clear, and colorless; soluble in benzene, acetone, and ether. Molecular weight (average) 1930 (cryoscopically; benzene). Elementary analysis:

Found %: Si 24.6, 24.6; C 63.1, 62.7; H 12.2, 12.1. $-\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. Calculated %: Si 24.6; C 63.1; H 12.3.

Using a small amount of AlBr_3 (up to 0.3 mole %) or $(\text{C}_2\text{H}_5)_3\text{Br}_3\text{Al}_2$ (up to 15.0 mole %) polymerization did not occur even with 4-8 hr boiling of the mixture. The use of 2-5 mole % AlCl_3 in this reaction led to formation of an analogous polymer. Longer heating of the reaction mixture at temperatures above 120-130° led to what was probably a structurally linear polymer such as we found previously [2]. Thus, on carrying out the reaction between 4.15 g of $(\text{CH}_3)_2\text{Si}(\text{CH}_2)_4$ and 0.17 g of AlCl_3 at 150-160° a rubbery polymer was formed. After it was ground, this only partly dissolved in boiling benzene. After the usual treatment of the benzene extract and vacuum treatment of the polymer at 110-120° (5 mm) we obtained 0.8 g of a yellow, viscous substance. Molecular weight 950 (cryoscopically; benzene).

Found %: Si 24.3, 24.4; C 63.6, 63.8; H 12.2, 12.4. $\text{SiC}_6\text{H}_{14}$. Calculated %: Si 24.6; C 63.1; H 12.3.

The rest of the polymer was a rubbery, insoluble substance.

Polycondensation of 1,4-hexamethyldisilylbutane. In a flask with a descending condenser was placed 26 g of $(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2$, and AlBr_3 (10 mole %) was added; the temperature of the mixture then rose by 5-6°. When the mixture was heated (80-83° in the flask) tetramethyl silane (b. p. 26-27°, n_D^{20} 1.3600) distilled off. When the weight of the condensate reached 10.9 g, the reaction mixture at once changed from a mobile liquid to a clear, rubbery substance, and heating was stopped. The weight of substance remaining in the flask was 18.7 g. The ground polymer was treated with hot ether and then with water. After the usual treatment of the ether extract we obtained 3.5 g of viscous, light yellow polymer. Molecular weight 850 (cryoscopically; benzene).

Found %: Si 25.2; C 62.6; H 12.2. $\text{SiC}_6\text{H}_{14}$. Calculated %: Si 24.6; C 63.1; H 12.3.

The remaining portion was a colorless, insoluble, rubberlike polymer.

In conclusion we express our thanks to Yu. P. Egorov and E. D. Lubush for running the spectral analysis in the present work.

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STUDY OF THE PHASE EQUILIBRIUM IN THE SYSTEM Ti_3Sn-Zr

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It has been shown [1, 2] that in the binary system titanium-tin between the low temperature modification of titanium and the chemical compound Ti_3Sn there is formed a continuous series of solid solutions. Here there is noted a very favorable ratio between the atomic radii in the lattice of α -Ti and Ti_3Sn (for coordination number 12). It is known that zirconium is a close analog of titanium; between both the α - and β -modifications of zirconium and titanium there exists an unlimited mutual solubility [3]. Comparative analysis of the structure of α -Zr and Ti_3Sn shows that they also satisfy the basic requirements [4] for forming a continuous series of solid solutions.

In this connection it is of theoretical interest to study the phase equilibrium in alloys whose figurative points lie on the Ti_3Sn -Zr section of the concentration triangle Ti-Zr-Sn.

From the practical point of view this investigation is useful in connection with the possibility of finding new compositions of alloys which will have interesting physicochemical properties. For carrying out the work proposed we have prepared alloys of zirconium with the compound Ti_3Sn . The composition of the alloys from the data of chemical analysis is given in Table 1.

As starting materials for preparation of the alloys we used magnesium thermal titanium TG-00 (99.8% Ti), zirconium from the iodide (99.9% Zr) and an alloy of Ti-Sn which contained 67.5% tin. The alloy was prepared by the method of induction fusion, without a crucible, of a weighed composition [5]. This was a more favorable method for preparing the alloy in studying the composition diagram since it permitted more marked shortening of the time of homogenizing tempering for bringing it to equilibrium [6].

The cast alloys were submitted to deformation (by about 20%) (after excluding alloys close in composition to the compound Ti_3Sn) and homogenizing tempering at 800°. The samples were placed in quartz ampules evacuated to 10^{-4} mm Hg and sealed. To prevent diffusion of air through the quartz the ampules with the samples were sealed in an evacuated ampule of greater diameter, and in the space between the ampules pure titanium sponge was placed as a getter. Such a method completely excluded the possibility of introducing gaseous impurities into the alloys during tempering. The homogenized alloys were studied under the microscope. As the etching agent to disclose the microstructure we used a mixture composed of one part HNO_3 , one part HF, and two parts of glycerol (by volume).

Microscopic analysis of the alloys after tempering for 1500 hr at 800° showed that they are all monophasic and have a polyhedral structure. This shows the existence of a continuous series of solid solutions between α -zirconium and the compound Ti_3Sn . After tempering at 800° all the alloys were successively tempered at 1000° and 1200° for 150 and 200 hr respectively and hardened from these temperatures in water. Microscopic analysis of the hardened samples gave the following picture of phase equilibrium in the system studied at these temperatures. Up to about 22 weight % zirconium, all the alloys are monophasic and have a polyhedral structure, almost the same as that which occurs with tempering at 800°. Beginning with this concentration, further increase

TABLE 1

Chemical Composition of Alloys Studied (in weight %)

Alloy No.	Ti	Zr	Sn	Alloy No.	Ti	Zr	Sn
1	51.9	4.9	43.2	9	27.6	49.9	22.5
2	49.2	10.0	40.8	10	24.4	55.0	20.6
3	47.2	14.7	38.1	11	19.6	64.3	16.1
4	44.2	19.9	35.9	12	14.6	74.0	11.4
5	40.8	25.0	34.2	13	11.9	79.2	8.9
6	37.4	30.1	32.5	14	8.4	84.6	7.0
7	32.9	39.9	27.2	15	5.5	89.4	5.1
8	30.3	44.8	24.9	16	3.4	94.1	2.5



Fig. 1. Microstructures of some alloys of the system Ti_3Sn-Zr after tempering and hardening in water. a) 30 weight % Zr at 800° (polyhedral structure γ (α)); b) 30 weight % Zr at 1000° (diphase structure $\gamma + \beta$); c) 50 weight % Zr at 1000° (diphase structure $\gamma + \beta$); d) 80 weight % Zr at 1000° (monophase needle structure α'). 200 x.

in zirconium concentration leads to the appearance of a second phase in the structure of the alloys, the amount of which increases regularly. Beginning at about 55% zirconium, the second phase has the α' structure. The alloys hardened at 1000° and 1200° which contain 80% weight % and more Zr had a monophase α' structure. In Fig. 1 are photomicrographs of some of the alloys to illustrate the descriptions of phase equilibrium in the system Ti_3Sn-Zr .

In Fig. 2 we give the relation of hardness to composition of alloys of Ti_3Sn-Zr hardened after tempering at 800, 1000, and 1200°. Hardness measurements were run on a Vickers apparatus with a load of 10 kg. It follows from Fig. 2 that the relation of hardness to composition of alloys hardened from 800° (curve 1) is characterized by a smooth curve with a maximum and is typical for a system with a continuous series of solid solutions, while the analogous relation for alloys hardened from 1000 and 1200° (curves 2 and 3) is characterized by a break in solubility, and in the diphase region the hardness changes practically in accord with the law of additivity. The break in the curve of relation of hardness to composition of alloys hardened from 1000 and 1200° allows us to locate the boundaries which separate the region of γ and $\gamma + \beta$, and also $\gamma + \beta$ and β .

On the basis of the data of microscopic analysis, and also from hardness measurements, we can conclude that the section Ti_3Sn-Zr of the ternary system $Ti-Zr-Sn$ is quasibinary.

For construction of the quasibinary diagram of state of Ti_3Sn-Zr we used the method of high-temperature thermal analysis without contact, distinguished by high sensitivity and permitting determination of the temperature of phase transformation up to 3000° [7-9].

Alloy samples with weight 1-2 g were placed in a crucible of zirconium oxide. Heating was carried out in an atmosphere of purified helium, which was introduced into the furnace chamber after pumping out to about

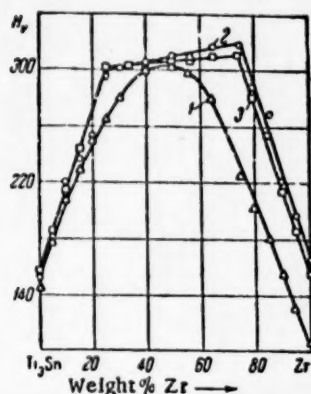


Fig. 2. Relation of hardness to composition of alloys of Ti_3Sn-Zr after tempering at 800, 1000, and 1200° and hardening in water (curves 1, 2, and 3 respectively).

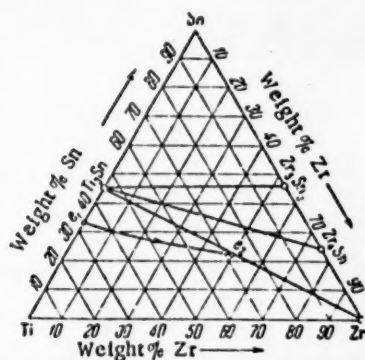


Fig. 4. Triangulation of ternary system titanium-zirconium-tin.

It should be noted that up to the present time the liquidus line in the diagram of state on the basis of titanium and zirconium has scarcely been constructed, because of the difficulty in carrying out thermal analysis of such high-temperature and chemically active materials. Therefore in the reference literature in the diagrams of titanium and zirconium the liquidus lines are usually dotted.

Use of thermographs without contact in this case permits, in addition to determination of solidus point and phase transformation in the solid state, also fixation of the liquidus temperature which corresponds to the separation of the first crystals of γ and β forms.

It follows from Fig. 3 that equilibrium between the β -modification of zirconium and the compound Ti_3Sn is shown on the diagram of state as a eutectic type with limited solubility in the solid state. The temperature of eutectic transformation is about 1540°; the concentration of the eutectic point is about 50 weight % Zr. Between the α -modification of zirconium and the compound Ti_3Sn there is formed a continuous series of solid solutions.

If we compare this diagram of Ti_3Sn-Zr with the diagram of Ti_3Sn-Ti then we see at once the similar geometrical form which describes the phase equilibrium in these systems; this shows to a considerable degree the far-reaching chemical analogy between titanium and zirconium. However, it should be noted that to reach equilibrium

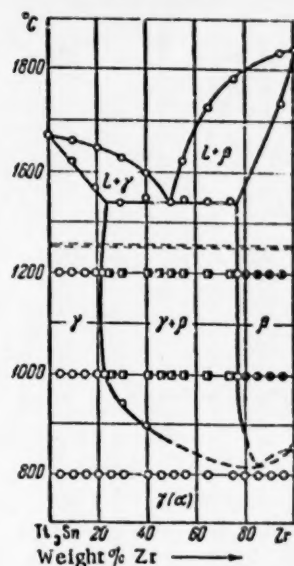


Fig. 3. Quasibinary diagram of state Ti_3Sn-Zr .

10^{-5} mm Hg. The record of the thermogram was made on coordinates of difference in temperature of sample and standard against time. On the thermogram taken with the alloys Ti_3Sn-Zr it was noted that as a rule there were two heat effects. In alloys containing 30.1 and 39.9 weight % Zr there were three heat effects, and in alloys with 49.9% Zr, only one heat effect at 1540°.

In Table 2 we give the temperatures observed on the thermogram of heat effects in the Ti_3Sn-Zr alloys studied.

On these data and also on the data of the study of microstructure and hardness of the alloys we have constructed the equilibrium quasibinary diagram of Ti_3Sn-Zr as shown in Fig. 3.

TABLE 2

Temperature of Phase Transformations
in Alloys of Ti_3Sn-Zr (in $^{\circ}C$)

Alloy composition, weight, %	I	II	III
10	1660	1620	—
19.9	1648	1565	—
30.1	1627	1540	1000
39.9	1600	1545	895
49.9	—	1540	—
55.0	1620	1543	—
64.3	1700	1540	—
74.0	1780	1542	—
94.1	1835	1731	—

and obtain all the alloys monophasic at 800° in the system Ti_3Sn-Ti requires very long homogenizing tempering, while in the system Ti_3Sn-Zr equilibrium is reached much more easily. This evidently shows that the rate of diffusion in the system Ti_3Sn-Zr at this temperature is considerably higher.

On the basis of the fact that the cross section investigated for Ti_3Sn-Zr in the ternary diagram of state of $Ti-Zr-Sn$ is quasi-binary, it is possible to triangulate this system [10, 11] (see Fig. 4). The figurative point which corresponds to the compound Ti_3Sn in this part of the diagram is nodal. Hence, aside from the section Ti_3Sn-Zr there should probably actually be sections Ti_3Sn-Zr_2Sn and $Ti_3Sn-Zr_3Sn_2$. The part of the diagram of state $Ti-Zr-Sn$ included in the triangle $Ti-Ti_3Sn-Zr$ at low temperature appears as continuous solid solutions. At higher temperatures, evidently, there will be a break in solubility and equilibrium becomes diphasic:

$\gamma + \beta$, on which the structure, depending on the concentration of the alloy, should be either $\gamma + \text{eutectic } (\gamma + \beta)$, or $\beta + \text{eutectic } (\gamma + \beta)$.*

Thus, by the methods of microscopic and thermal analysis and also by measuring the hardness of the alloys we have studied phase equilibrium in the system Ti_3Sn-Zr ; we have shown that the system Ti_3Sn-Zr is quasi-binary; on the basis of general theoretical considerations we have shown the existence of a continuous series of solid solutions between the low-temperature modification of zirconium and the compound Ti_3Sn . We have carried out triangulation of the ternary system titanium-zirconium-tin, as a result of which further treatment of this system will be made considerably easier.

In conclusion we express thanks to the author of the method of thermography without contact, N. A. Nedumov, for help in carrying out the thermal analysis of the alloys of this system.

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*This appears in the structure after crystallization, since after heating the monophasic alloy at low temperature the eutectic structure is absent and there appears only the corresponding second phase.

BINARY SYSTEMS OF MOLECULES WITH TWO RINGS INCLUDING THIONAPHTHENE

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(Presented by Academician I. I. Chemyaev, July 1, 1960)

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Phase equilibria in systems which include thionaphthene are scarcely to be found in the literature. It is of interest to determine the type of phase diagram in combinations of thionaphthene with such second components as are very close to it in the structure of the molecule skeleton (indene, indole) or which differ from it regularly (isoquinoline, 2-methylnaphthalene, 3-methylisoquinoline, 2,6-dimethylnaphthalene). The presence of the selected substances in coal and the products of oil treatment determined the applied direction of this work.

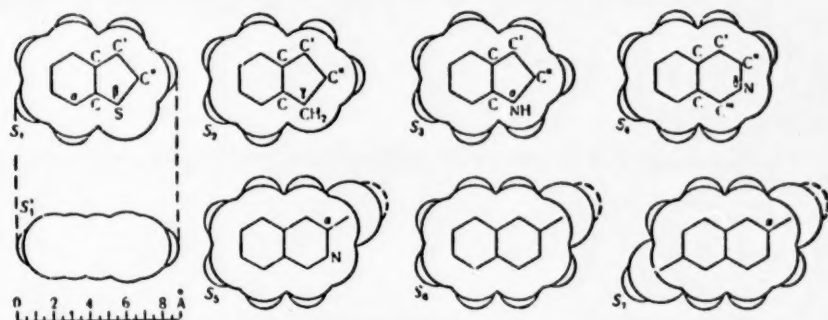


Fig. 1. Sections of the molecule models; S_1 and S_1' - thionaphthene; S_2 - indene; S_3 - indole; S_4 - isoquinoline; S_5 - 3-methylisoquinoline; S_6 - 2-methylnaphthalene; S_7 - 2,6-dimethylnaphthalene.

Components of the systems. Thionaphthene and 2-methylnaphthalene were synthetic, and the other five substances were of coke chemical origin. All substances were carefully purified. As a result of the preparation we obtained substances with melting point and crystallization within ± 0.1 , as shown in the table.

Method of study of the binary systems. We used four methods. The relation of T and X between the composition X (in percent) of the mixture and the equilibrium temperature T of the condensed phase was determined: a) by thermal analysis in an apparatus assembled according to [1]; b) by visual observations on the same laboratory apparatus; c) by a series of mixtures specially made up and studied with a dilatometer in an ultrathermostat of the Wobbers type; d) the behavior of the components in the liquid phase was determined from the index of refraction n_D for mixtures of composition X in an Abbe refractometer.

The type of phase diagram established by the experiments, continuous solid solutions and eutectic systems, fitted in well with the structural characteristics of the components; in Fig. 1 we give sections of the molecule models.

Binary Systems of Thionaphthene (X_w , weight %, X_m , mole % thionaphthene, t_i temperature of initial crystallization, t_s end of crystallization)

X_w	X_m	t_i	t_s	X_w	X_m	t_i	t_s	X_w	X_m	t_i	t_s
Thionaphthene-Indene											
100.00	100.0	31.2	—	56.46	52.9	18.0	15	18.43	16.4	4.2	2
89.47	88.1	28.1	27	48.84	45.3	15.2	12	10.14	9.0	1.0	0
80.79	78.5	25.6	24	42.90	39.4	13.1	10	4.75	4.1	-0.2	-1
73.91	71.1	23.6	22	26.61	23.9	6.9	5	0.00	0.0	-1.7	—
67.22	64.0	21.6	19								
Thionaphthene-Indole											
100.00	100.0	31.2	—	67.33	64.3	31.1	33	22.90	20.5	42.5	40
93.25	92.3	31.6	31	59.60	56.3	35.0	34	13.42	11.9	46.5	43
87.38	85.8	31.9	31	44.14	40.8	37.0	35	6.09	5.3	49.8	47
75.60	73.0	33.3	32	34.79	31.7	39.0	37	0.00	0.0	53.0	—
Thionaphthene-Isoquinoline											
100.00	100.0	31.2	—	46.70	45.8	27.8	26	21.53	20.9	26.6	—
91.56	91.2	30.2	29	33.16	32.6	27.2	25	15.36	14.8	26.1	24.5
78.30	77.7	29.6	28	14.90	14.0	28.8	—	4.10	4.0	25.1	24
70.16	69.4	29.2	27.5	58.21	57.3	28.6	27	0.00	0.0	24.7	—
Thionaphthene-2-methylnaphthalene											
100.00	100.0	31.2	—	60.10	61.5	-4.2	-4.2	21.10	22.1	19.5	-4.2
88.37	88.9	33.0	-6	54.78	56.2	-1.1	-4.2	12.65	13.3	25.2	-4.2
79.43	80.4	15.8	-5	40.48	51.5	1.8	-4.2	6.24	6.6	30.0	-5
73.48	74.6	10.3	-4.2	43.21	45.6	5.9	-4.2	0.00	0.0	34.4	—
69.50	70.8	6.7	-4.2	31.55	32.8	13.0	-4.2				
Thionaphthene-3-methylisoquinoline											
100.00	100.0	31.2	—	73.04	74.4	13.2	13.2	42.81	44.4	39.9	13.2
93.81	91.2	27.7	13	69.94	71.3	16.1	13.2	31.76	33.2	47.8	—
89.16	89.8	24.1	13	66.40	67.8	20.0	13.2	20.37	21.5	54.6	—
83.37	84.3	20.8	13.2	56.56	58.2	24.2	13.2	9.58	10.7	60.4	—
78.07	79.2	17.0	13.2	47.54	49.2	36.0	13	0.00	0.0	65.7	—
75.55	76.6	14.9	13.2								
Thionaphthene-2,6-dimethylnaphthalene											
100.00	100.0	31.2	—	78.30	80.8	41.2	22.5	57.10	55.9	81.5	22
96.40	96.9	28.1	22.5	73.25	76.1	48.0	22.5	33.13	36.7	84.5	22
93.19	94.1	26.0	22.5	64.37	67.8	59.9	22.5	18.27	20.7	99.1	—
90.24	92.2	24.1	22.5	54.96	58.7	70.2	22.5	9.31	10.6	105.0	—
88.65	90.1	22.5	22.5	47.71	51.5	77.0	22	0.00	0.0	110.0	—
83.54	85.6	32.5	22.5								

In the original literature structural measurements are described for 2,6-dimethylnaphthalene; the models of the other six molecules in Fig. 1 are constructed from averaged or approximate data, with calculations from [2, 3]. The atom centers of the skeletons of the molecules are distributed in one plane. The valence bonds and angles used are: a) in benzene and naphthalene rings: CC 1.4, CH 1.08 Å, $\angle \alpha$ 120°; b) in 5-membered thionaphthene ring, from thiophene [4]: C'C* - 1.35; CC* 1.44; CS 1.74; CH 1.08 Å; $\angle \beta$ 91°; $\angle \text{SC}^*\text{C}'$ 112°; $\angle \text{C}^*\text{C}'\text{C}$ 113°; c) in the 5-membered indene ring, from fluorene [5]: CC' 1.50, C'C* 1.40; C'CH₂ 1.52 Å; $\angle \gamma$ 106°; $\angle \text{CC}'\text{C}^*$ 108°; $\angle \text{C}'\text{C}^*\text{CH}_2$ 109°; d) in the 5-membered indole ring, from pyrrole [6]: CC' 1.44, C'C* 1.55 Å; C 1.42, $\angle \sigma$ 108°; $\angle \text{CC}'\text{C}^*$ 108°; $\angle \text{C}'\text{C}^*$ 110°; e) nitrogen ring in isoquinoline and 3-methylisoquinoline, from pyridine [6]: C'C* 1.39; C*N 1.37 Å; $\angle \text{CC}'\text{C}^*$ 121°; $\angle \delta$ 119°.

The external contour of the molecule models in Fig. 1 is constructed by the use of intermolecular radii of approach (A): R_C 1.8, R_S 1.85, R_N 1.57, R_H 1.17; the contour of the hydrogen atoms in methyl is conditionally shown by the dotted line. As to the "thickness" of the molecule models, this on the average equals 2R_C, about 3.6 Å. Some "curvature" is noted for the region of the sulfur atom of thionaphthene, 2R_S, about 3.7 Å, and a corresponding less thickness for the nitrogen atom, 2R_N, about 3.2 Å. From the models we calculated the areas of the section S A² and the volume V A³ of the molecules; their ratios are given below.

The results of determination of temperature of phase equilibrium with change in composition for the six systems which include thionaphthene are given in the table. The corresponding phase diagrams of t and X are shown in Fig. 2, where we also give the line n_D , X (two dots-dash), one for each system.

System thionaphthene-Indene. We find continuous solid solutions. The mixture crystallized (melted) in a narrow temperature range, not exceeding 3°. On the phase diagram t , X , Fig. 2, 1, the line of initial crystallization occurs with very slight curvature (about 2° in the middle portion) to the limiting [7] straight line

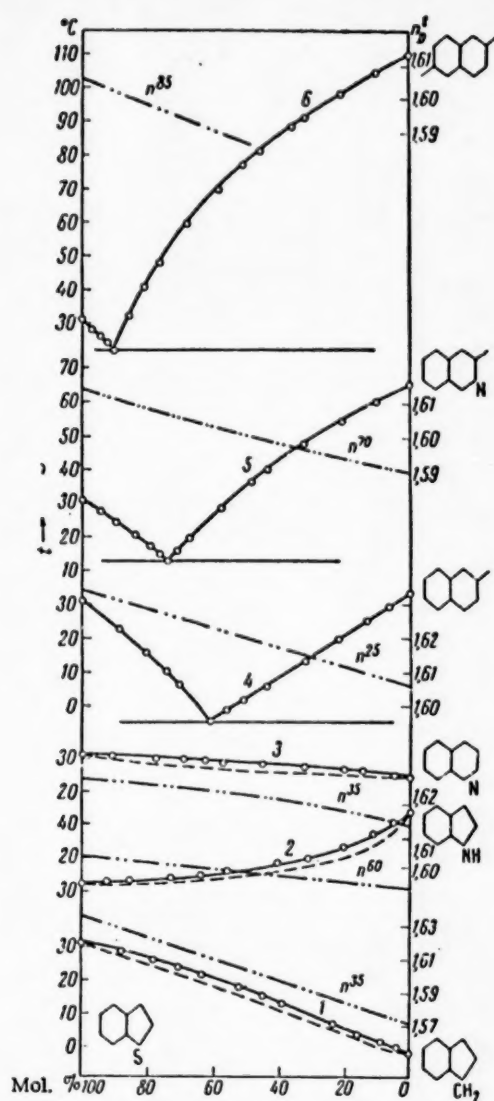


Fig. 2. Diagrams of t, X and n^t_D, X for systems of thionaphthene with indene (1), indole (2), isoquinoline (3), 2-methylnaphthalene (4), 3-methylisoquinoline (5), 2,6-dimethylnaphthalene (6).

System thionaphthene-2-methylnaphthalene, Fig. 2,4: t_e 4.2°, X_e 61.5 mole %, Δt thionaphthene about 2-3°, Δt 2-methylnaphthalene about 3-4°, ΔS about 18%, ΔV about 22%.

System thionaphthene-3-methylisoquinoline, Fig. 2,5: t_e 13.2°, X_e 74.4 mole %, Δt thionaphthene 6-8°, Δt 3-methylisoquinoline 8-10°, ΔS about 15%, ΔV about 19%.

System thionaphthene-2,6-dimethylnaphthalene, Fig. 2,6: t_e 22.5°, X_e 90.1 mole %, Δt of both components 2-3°, ΔS about 28%, ΔV about 36%.

Hence the eutectic type of the three thionaphthene-containing systems is explained by the considerably different form (Fig. 1) and dimensions of the molecules of the compounds: $\Delta S > 14\%$ and $\Delta V > 20\%$.

which can be drawn between the melting points of the components. The scarcely concave line of end of crystallization is equally close to the limit. The ratio of structural characteristics of the components is: S_1/S_2 about 1.4; V_1/V_2 about 1.1. The diagram of $n^{60}D$ for Fig. 2,1 is linear, type I according to V. Ya. Anosov [8].

System thionaphthene-indole, In Fig. 2,2 we give the diagram t, X which is characteristic for a series of continuous solid solutions with the greatest difference between temperature of beginning and ending of crystallization of about 4° at a thionaphthene concentration of about 15%. The lines of beginning and ending of crystallization are close to the limiting straight line and slightly curved (by 5-6° in the middle part). Here S_1/S_2 is about 1.05, V_1/V_2 about 10.6. The line of $n^{60}D$ is linear, type L.

The system thionaphthene-isoquinoline (Fig. 2,3) shows a continuous series of solid solutions. The lines of beginning and ending of crystallization, correspondingly convex and concave, are symmetrically arranged on either side of the limiting straight line, the variation from which in the middle part is about 1°. As a whole the t, X diagram is a very narrow "cigar" which lies almost horizontal, since the melting points of the components differ by 6° in all. Here S_1/S_4 is about 1.03, V_1/V_4 about 1.05 and is connected with the "convexity" of thionaphthene and the "concavity" of isoquinoline. The line $n^{35}D$ is nearly straight.

Thus, in two of the three thionaphthene-containing systems we find the very rare type of phase diagram illustrated by the approach of the line t, X to the linear limit, where the continuous solid solutions occur with participation of a structurally close second component, at ΔS about 3-5% and ΔV about 1-6%.

The three systems of thionaphthene with homologs of naphthalene and isoquinoline are eutectics. For them, as a rule, there is a second eutectic break on the temperature-time curve, corresponding to the t, X diagram. We give the coordinates of the eutectic point: temperature (t_e , °C) and thionaphthene content (X_e , mole %) and indicate the observed supercooling (Δt , °C) of the components which are crystallized with intensive stirring, and we note the ratio of ΔS and ΔV of the components.

The earlier studied system thionaphthene-naphthalene is characterized by a phase diagram t, X [9] whose type can be considered intermediate between the eutectic and solid solution types described in the present paper. The diagrams of n^D for the eutectic thionaphthene-containing systems studied in Fig. 2, 4-6 are very close to linear, type I; that is, there is no reaction of the components in the liquid phase.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

DIETHYL-Se-CHLOROSELENOPHOSPHATES

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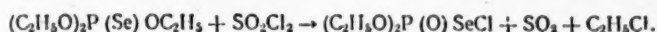
(Presented by Academician M. I. Kabachnik, June 28, 1960)

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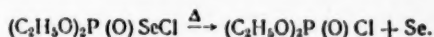
Original article submitted June 24, 1960

Several years ago in our laboratory we obtained a new type of organic phosphorus compound which contained the group of atoms $>P(O)SCl$. These compounds were obtained by the action of chlorine or sulfonyl chloride on dialkylmonothiophosphates [1-5] and also on dialkoxylphosphinyldisulfides [1, 2, 6] and trialkylthione phosphates [7]. The resulting substances had great chemical activity. As typical thiophosphorylating reagents with an electrophilic character, they easily added to unsaturated compounds [8-10], giving the reaction of electrophilic aromatic substitution [11], substituting hydrogen atoms in active methylene groups [1, 12], and reacting with other typical nucleophilic reagents: mercaptans and thioacids [13], amines [11], trialkyl- and dialkylphosphites [12], and similar substances.

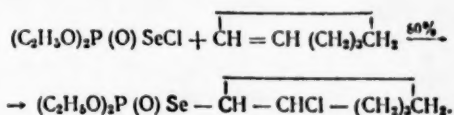
The subject of the present communication is a set of experiments leading to the preparation of the selenium analogs of these compounds. Diethyl-Se-chloroselenophosphates are formed by the action of chlorinating agents on esters of selenoacids of phosphorus, fully analogously to the sulfur compounds. However, we could not isolate these substances in the pure form since they were easily decomposed. They were more stable in solution. Thus diethyl-Se-chloroselenophosphate, formed by the action of equivalent amounts of sulfonyl chloride on triethylselenophosphate in benzene solution at -5° , is relatively stable and in this form can be used for further reactions:



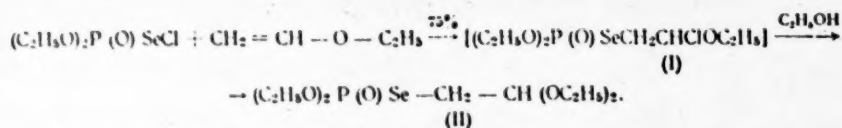
Complete distillation of the solvent leads to decomposition of the substance with evolution of selenium:



Diethyl-Se-chloroselenophosphate is decomposed in the presence of the least trace of water, but in other reactions it is a less active compound than the corresponding diethyl-S-chlorothiophosphate. Its addition to cyclohexene, chosen as an example of the addition reaction to ethyl hydrocarbons, goes much more slowly than in the case of the thio analog:



The reaction of addition of diethyl-Se-chloroselenophosphate to ethylvinyl ether also goes relatively slowly. The addition product (I), however, was not isolated, due to its instability, but we isolated the product of its reaction with ethyl alcohol, the stable acetal (II):

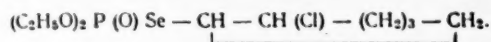


The ease of formation of the acetal can be considered confirmation of the suggested direction of the addition reaction.

EXPERIMENTAL

1. Diethyl-Se-chloroselenophosphate $(C_2H_5O)_2P(O)SeCl$. To a solution of triethylselenophosphate (15.9 g, 0.065 mole) in benzene (1:1) was added dropwise a solution of sulfuryl chloride (8.8 g, 0.065 mole) in benzene (1:1), and the temperature of the exothermal reaction was kept below 0° . The originally colorless solution gradually became yellow. After addition of all the sulfuryl chloride, the volatile reaction products were distilled at reduced pressure (about 1 hr). Attempts to distill the benzene completely on a water bath heated to 30° led to decomposition of the product and formation of selenium. In the following experiments diethyl-Se-chloroselenophosphate was not isolated and was used for further reactions in the form of a benzene solution.

2. Reaction of addition of diethyl-Se-chloroselenophosphate to cyclohexene. O,O-Diethyl-Se-(2-chlorocyclohexyl)-selenophosphate



To the benzene solution of diethyl-Se-chloroselenophosphate obtained as in experiment 1 was added dropwise a solution of cyclohexene (6.6 g, 0.08 mole) in benzene (1:1), and the temperature of the weakly exothermic reaction was kept below 20° . Decolorization of the reaction mixture occurred only after standing for 3 days at room temperature. The volatile products were distilled at reduced pressure. The benzene solution was washed with sodium bicarbonate and water and was dried over $MgSO_4$. The benzene was distilled off at reduced pressure. We obtained 15 g of O,O-diethyl-Se-(2-chlorocyclohexyl)-selenophosphate as a colorless oil (69.3% of theoretical with respect to the starting triethylselenophosphate); b. p. $93-94^\circ/0.07$ mm, n_D^{20} 1.5166.

Found %: P 9.5; Se 23.5. $C_{10}H_{20}O_3ClPSe$. Calculated %: P 9.3; Se 23.7.

3. Reaction of addition of diethyl-Se-chloroselenophosphate to vinyl ethyl ether. O,O-Diethyl-Se-(2,2-diethoxyethyl)-selenophosphate $(C_2H_5O)_2P(O)SeCH_2CH(OC_2H_5)_2$.

To a benzene solution of diethyl-Se-chloroselenophosphate obtained as in experiment 1 was added dropwise a solution of vinyl ethyl ether (5.8 g, 0.08 mole) in benzene (1:1); the temperature of the weakly exothermic reaction was kept below 0° . After addition of all the diethyl-Se-chloroselenophosphate the solution was not decolorized. Full decolorization occurred only after 24-hr standing at room temperature. The solvent was distilled off at reduced pressure. To the oily residue of O,O-diethyl-Se-(2-ethoxy-2-chloroethyl)-selenophosphate, ethyl alcohol was added (25 ml); then the reaction mixture was left for $\frac{1}{2}$ hr at room temperature and was neutralized with solid sodium bicarbonate. The liquid was decanted from the precipitate and the residue was washed twice with benzene. The benzene extract was combined with the oil, washed twice with water, and dried with $MgSO_4$. The benzene was distilled off in a vacuum and the residue was fractionated. We obtained 17 g of O,O-diethyl-Se-(2,2-diethoxyethyl)-selenophosphate in the form of a thick, light yellow mass (78.7% of theoretical with respect to the starting triethylselenophosphate); b. p. $81-81.5^\circ/0.05$ mm; n_D^{20} 1.4710.

Found %: P 9.5; Se 23.4. $C_{10}H_{22}O_5PSe$. Calculated %: P 9.3; Se 23.7.

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THE SYNTHESIS OF COMPLEX FLUORIDES OF HEXAVALENT RHENIUM

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(Presented by Academician I. V. Tananayev, July 7, 1960)

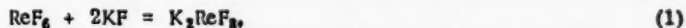
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 1, pp. 111-113, January, 1961

Original article submitted June 4, 1960

Complex salts of hexavalent rhenium have not been described up to the present time. I. Noddak and W. Noddak [1] reported the preparation of a solution of an oxychloroacid of rhenium-VI and its potassium salt, but in view of the very great instability of this compound in water it was not isolated from solution. The reason for the instability of compounds of hexavalent rhenium in water solution is their easy hydrolysis with later disproportionation according to the scheme $3\text{Re}^{\text{VI}} \rightarrow \text{Re}^{\text{IV}} + 2\text{Re}^{\text{VII}}$. The same authors reported only the isolation of a thiocyanate salt with the composition $\text{C}_5\text{H}_5\text{NHNCS} \cdot \text{ReO}(\text{CNS})_4$.

Hargreaves and Peacock [2] recently reported the reaction of rhenium hexafluoride with potassium fluoride in solution of iodine pentafluoride or liquid SO_2 . The authors say that there is then formed potassium octafluororhenate, K_2ReF_8 . However, chemical analysis of the isolated substance differs from this formula, and the Debyeogram shows the presence in it of potassium fluoride.

In the present work we have succeeded in carrying out the synthesis of potassium octafluororhenate by direct reaction between liquid rhenium hexafluoride and potassium fluoride. The reaction was carried out in a Teflon tube in which was placed 25 g of rhenium hexafluoride obtained by fluorination of the metal with chlorine trifluoride by the process which we have described [3]. Then, with cooling, we added small portions of finely ground potassium fluoride (6.54 g). The operation was carried out in a dry chamber cooled below zero. The reaction between these reagents occurred with considerable heating. When all the KF had been added to the tube, the latter was tightly sealed and heated to 20°C . After standing for 12 hr at this temperature, the reaction was complete. The excess rhenium hexafluoride was removed by distillation in a vacuum, and the resulting product was again finely ground and repeatedly treated with 2-3 g of ReF_6 , after which the volatile part was again pumped off in a vacuum. The results of analysis of the product before and after the repeated treatments showed a constant composition. All the resulting product (23.4 g) accorded with the calculation for the equation



starting from the potassium fluoride used. The product which was obtained contained a small amount of adsorbed ReF_6 , had a cream color, and was violently decomposed by water with formation of a black precipitate.

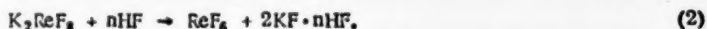
In the general mass of the products we found moderately large crystals of a crimson color. These crystals were practically insoluble in water and were decomposed very slowly by it, giving a soluble product. Because of these properties with respect to water, the crimson crystals could be isolated in pure form by treating the product from the reaction of rhenium hexafluoride and KF by the above method with ice water. However, to obtain the crimson salt by this method it was necessary to make changes, avoiding excess rhenium hexafluoride and taking equivalent amounts of the starting substances. In this case we obtained a product with a crimson color which consisted almost entirely of potassium octafluororhenate. In order to purify this product from admixed potassium fluoride, it was washed with ice water and methyl alcohol and dried in a vacuum. Chemical analysis confirmed that the composition of the crimson salt corresponded to the formula K_2ReF_8 .



In the figure we give a representation of a crystal of potassium octafluororhenate. In the plane of the drawing the crystal is biaxial, has direct extinction, and hence belongs to the rhombic syngony. The extension of the crystals is positive.

The potassium octafluororhenate is sufficiently stable in air and begins to decompose only after several hours; its bright crimson color fades and turns blue, after which it rapidly becomes black. The potassium octafluororhenate is practically insoluble in water, but it slowly hydrolyzes to form a blue product which dissolves in water with formation of a blue solution. Hot water dissolves the octafluororhenate with formation of a green solution which soon takes on a brown color due to hydrolysis. The salt keeps well in polyethylene ampules. When kept in glass, it quickly decomposes, corroding the surface of the glass.

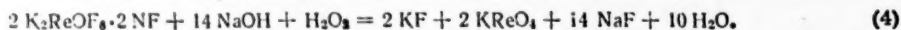
Potassium octafluororhenate dissolves in hydrogen fluoride with decomposition to evolve rhenium hexafluoride according to the scheme:



Rhenium hexafluoride itself has limited solubility in hydrogen fluoride with formation of a colorless solution. When such a solution is evaporated in a stream of dry hydrogen, rhenium hexafluoride is volatilized along with the hydrogen fluoride, and in the residue there remains a saturated solution of potassium fluoride in hydrogen fluoride from which crystals of the acid fluoride separate. The combined condensates after removal of hydrogen fluoride from them in a vacuum at -70° are used again for obtaining potassium octafluororhenate.

As was shown above, potassium octafluororhenate slowly reacts with water to form a blue product. However, in view of the rapid decomposition of this product it was not possible to isolate it from water solution. A compound with the same blue color could be isolated from the hydrogen fluoride solution. It was observed that the solution of K_2ReF_8 in HF on standing in air took on a blue color, and the solid phase consisting of rhenium hexafluoride in accord with Eq. (2) dissolved entirely. When K_2ReF_8 dissolved in HF which contained a little water (0.02%) we obtained a clear blue solution from which after cooling to -70° a blue, crystalline substance separated. The solution was then decanted; the remaining hydrogen fluoride was removed from the solid residue in a vacuum. The blue product had a homogeneous crystalline structure whose composition corresponded to the formula $\text{K}_2\text{ReOF}_6 \cdot 2\text{HF}$ and was potassium oxyhexafluororhenate with two molecules of HF. In water at 0° this salt appreciably dissolved with formation of a blue solution which after 10 min turned green and then quickly took on a brown color. The potassium oxyhexafluororhenate easily dissolved in hydrogen fluoride, and when water was added to this solution the blue color turned green and then brown. When the green solution was cooled, large green crystals precipitated. Although they were not analyzed, we could still assume that this salt was the product of further hydrolysis of potassium oxyhexafluororhenate, for example to $\text{K}_2\text{ReO}_2\text{F}_4$.

The method of analysis, as was described for analysis of rhenium hexafluoride [2], was based on hydrolysis of a sample with a known amount of alkali, with simultaneous oxidation with hydrogen peroxide. The excess alkali was titrated. Calculation of the alkali required for the neutralization was carried out by the equations:



In the table we give the results of calculations of the required amount of alkali in gram-equivalents per 1 g of salt and the amounts obtained. Further, we determined rhenium in the solution in the form of nitron per-rhenate and fluorine by titration with AlCl_3 solution. Potassium was determined in the form of sulfate in the solution after removal of rhenium as the sulfide.

Potassium octafluororhenate is the analog of complex compounds based on hexafluorides of molybdenum, tungsten, and uranium, for which Martin and Albers [4] and Cox, Sharp, and Sharp [5] synthesized potassium salts with the composition K_2MeF_8 , while for heavier cations were obtained salts with the composition MMOF_7 and MWF_7 [6], where M is rubidium or cesium. As to potassium oxyhexachlororhenate, there is at present a report [6] on the preparation of oxyfluoro salts of molybdenum and tungsten starting from the fluorooxides MeOF_4 and having the composition CsMoOF_6 and CsWOF_6 .

Data of Chemical Analysis of Complex Fluorides of Rhenium

Compound	K content, %		Re content, %		G-equiv. alkali		F content, %	
	found	calcd.	found	calcd.	found	calcd.	found	calcd.
K_7ReF_8 Potassium octa- fluororhenate (crimson salt) $K_7ReOF_8 \cdot 2HF$ Potassium oxyhexa- fluororhenate (blue salt)	18,6 $\pm 0,2$	18,8	44,6 $\pm 0,2$	44,7	0,165 $\pm 0,002$	0,168	36,2 $\pm 0,1$	36,4
	17,6 $\pm 0,2$	17,9	42,7 $\pm 0,2$	42,9	0,160 $\pm 0,001$	0,161	34,7 $\pm 0,2$	35,0

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THE STABILITY OF CHLORIDE ACIDOCOMPLEXES OF ELEMENTS OF THE FOURTH PERIOD

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(Presented by Academician I. I. Chernyaev, July 1, 1960)

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The investigation of the state of elements in hydrochloric acid solution by means of anion exchange has attracted much attention, since the sorption of elements with even similar properties is different due to differing stabilities of the chloride acidocomplexes [1]. However, there is very little information on the anion exchange properties of chloridocomplexes of elements of the fourth period [2-4].

In undertaking a systematic investigation of the state of the elements in the middle of the fourth period in hydrochloric acid solution [5], we have set ourselves the problem of making a detailed study of the stability of the chloride complexes of these elements by anion exchange.

We have studied the behavior of the elements Ti(IV), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) in solution with concentrations of HCl from 0.1 to 12 N. For this we have determined the distribution coefficient of the elements φ between the anion-exchange resin and the hydrochloric acid solution: An exact weight of air-dried anionite (0.5 g) was shaken with a determined volume of the solution studied (50 ml) until equilibrium was reached; we took an aliquot portion of the solution and determined the amount of element not sorbed on the resin by one of the colorimetric methods [6]. The distribution coefficient of the element φ was calculated in the usual way [5]. We also determined the sorbability of the element by the resin at equilibrium in percent of the original amount.

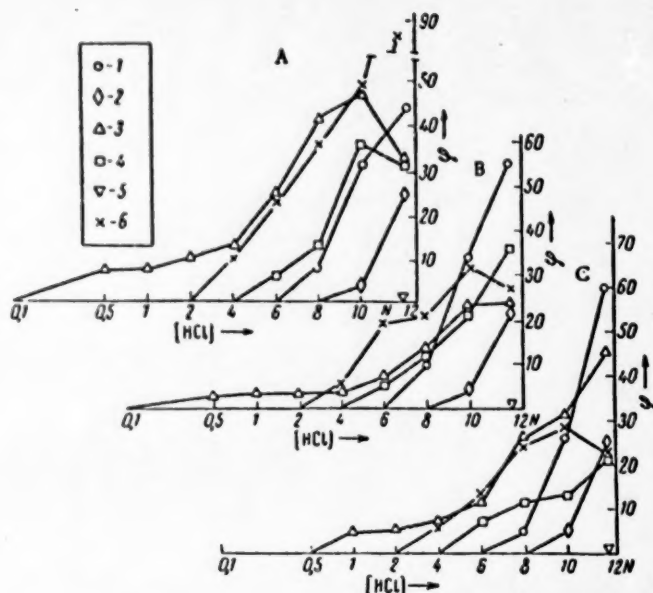
The starting solutions were prepared in twice-distilled water from chemically pure reagents and had the following concentrations: Ti 0.1197, Mn 0.2794, Fe 0.1861, Co 0.2947, Ni 0.2935, and Cu 0.4765 mg/ml.

For obtaining satisfactory results we used in the experiments three anion exchange resins of domestic manufacture: strongly basic anionite AV-16, medium basic ÉDE-10 P, and the weakly basic anionite AN-2F. In preparation for the study we sifted the fraction of all the anionites with grain diameter 0.5-1.0 mm; the anionites were washed free of admixtures, converted to the Cl form, and air dried.

The distribution coefficients of the elements between hydrochloric acid solutions and the strongly basic anionite AV-16 are shown in curve A of the figure. A sufficiently clearly shown adsorption of the elements by this anionite took place from solutions with the following concentrations of hydrochloric acid: Fe from 0.5 N, Cu from 4 N, Co from 6 N, Ti from 8 N, Mn from 10 N solutions of hydrochloric acids; Ni was not adsorbed by the resin at concentrations of hydrochloric acid from 0.1 to 12 N.

From the figure, B, C, it is clear that anionite ÉDE-10P and especially AN-2F as a whole have lower exchange abilities than AV-16. However, the adsorbability of the elements by these resins confirms well the observed regularities in the behavior of elements in hydrochloric acid solution.

It follows from our experimental data that a considerable amount of chloride anion complex is formed for Ti in about 8 N, for Mn in 10 N, for Fe in 0.5 N, for Co in 6 N, and for Cu in 4 N hydrochloric acid. Evidently



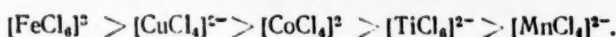
Relation of distribution coefficients of the elements to HCl concentration: A) anionite AV-16; B) anionite ÉDÉ-10P; C) anionite AN-2F. 1) Ti, 2) Mn, 3) Fe, 4) Co, 5) Ni, 6) Cu.

Sorbability of Elements by Anionites from Hydrochloric Acid Solutions

Normality of HCl	Adsorbed at equilibrium, %					
	Fe	Cu	Co	Ti	Mn	Ni
Anionite AV-16						
0.1	0	0	0	0	0	0
0.5	6.23	0	0	0	0	0
1	6.66	0	0	0	0	0
2	8.81	0	0	0	0	0
4	11.23	8.91	0	0	0	0
6	19.98	12.05	5.83	0	0	0
8	29.60	26.41	11.67	6.18	0	0
10	32.61	32.79	26.67	24.17	3.34	0
12	24.94	46.39	24.46	30.57	20.12	0
Anionite ÉPÉ-10P						
0.1	0	0	0	0	0	0
0.5	3.00	0	0	0	0	0
1	3.33	0	0	0	0	0
2	3.33	0	0	0	0	0
4	4.19	4.46	0	0	0	0
6	6.66	15.83	5.02	0	0	0
8	11.87	17.43	9.16	9.42	0	0
10	18.75	24.21	17.23	25.58	3.64	0
12	16.61	21.12	26.39	35.57	17.93	0
Anionite AN-2F						
0.1	0	0	0	0	0	0
0.5	0	0	0	0	0	0
1	4.62	0	0	0	0	0
2	5.05	0	0	0	0	0
4	5.85	5.57	0	0	0	0
6	11.28	11.67	6.67	0	0	0
8	19.61	19.20	9.46	4.76	0	0
10	23.75	21.65	11.67	20.55	5.02	0
12	30.81	17.78	17.57	37.51	18.71	0

at lower concentrations of hydrochloric acid solutions the chloridocomplexes of these elements are decomposed. A negatively charged complex of nickel practically does not exist under these conditions.

Thus, the chloride complexes of the elements of the fourth period which are formed in solutions of concentrations of hydrochloric acid from 0.1 to 12 N can be arranged in the following order of decreasing stability:



If in a dilute solution of electrolyte the sorbability of the elements is determined chiefly by the size of the charge or radius of the hydrated ions of equal valence, then in the case of the chloridocomplexes no such simple relationship evidently exists. Nonetheless, it is possible to connect the stability of the chloride anions complexes of the elements studied with their position in the periodic system.

A. A. Grinberg established the general proposition that in most periods the ability to form complexes is least at the boundaries and greatest in the middle; the maximum ability for complex formation agrees with this for elements in group VIII, since they have the most labile electron shells with unfilled d-nuclei [7]. It is also known that ions with 18 electrons and incomplete outer shells, with other conditions equal (size of charge and radius), are distinguished by stronger polarizing action and are more typical complex formers than are 8-electron ions.

The results of determination of the stability of the chloride acidocomplexes in elements of the fourth period on the whole agree well with these general ideas. Actually, the chloridocomplexes of iron and cobalt, which belong to group VIII, are very stable. Great stability also distinguishes the chloride complex of copper as an inserted element adjoining group VIII. The stability of the chloride anion complex for titanium and manganese is much weaker. The instability of the negatively charged complex for nickel under the conditions of our experiment can be explained by its conversion to a neutral complex.

In the table we give data on the adsorption of the elements by anionites from hydrochloric acid solutions in percentages. These show that the adsorption of these elements by the resins increases with increasing acidity of the solutions and even under static conditions reaches a considerable size. It is evident that this can be used in practice, the more so that under dynamic conditions (column chromatography) the effectiveness of the anionites increases still more.

The different stabilities of the chloride anion complexes in these elements can serve as a basis for separating them on anion-exchange resins. If the adsorption of the elements by anionites in hydrochloric acid solutions depends on formation of chloride anion complexes, then decreasing the concentration of hydrochloric acid in the wash column solution can give successive decompositions of these complexes and hence desorption of the elements. Repeated washing of the anion exchange resin with solutions of hydrochloric acid at progressively lower concentrations can give chromatographic separation of a mixture of elements. Thus, the domestic anion exchange resins AV-16, EDE-10P, and AN-2F can be used to various extents for separation of elements of the fourth period similarly to that for some of the elements of this period separated on anionite Dowex-1 [2]. There is also the possibility of separating pairs of elements of the fourth period in different combinations on the anionites.

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EFFECT OF ORGANIC SOLVENT ON THE SEPARATING POWER
OF α -HYDROXYISOBUTYRIC ACID

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January, 1961

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As we showed previously [1], the separating power of some monobasic α -hydroxy acids in chromatography depends to a large extent on their dissociation constants. With an increase in the strength of the proton bond in the acid there is also an increase in the strength of the complex bond of these acids with rare earth elements and a simultaneous increase in their separating power. The dielectric constant of the medium is known to have a strong effect on the degree of dissociation of acids. Therefore, it seemed interesting to study the change in stability of similar complexes in mixed solvents.

The properties of cerium and yttrium α -hydroxyisobutyrate complexes in dioxane-water mixtures were studied. Dioxane was convenient for this purpose as it is completely miscible with water and thus gives mixtures with a wide range of dielectric constants. We used α -hydroxyisobutyric acid which had been synthesized by hydrolysis of acetone cyanhydrin with hydrochloric acid. It was purified by recrystallization from benzene. The dioxane was distilled over sodium.

In our investigation we used tracer amounts of radioactive isotopes Y^{91} , Ce^{144} , Pm^{147} , and Nd^{147} of satisfactory radiochemical purity. In static experiments we used KII-2 ionite (with a grain size of 0.25-0.50 mm) in the sodium form) and for chromatographic separation, KRS-200 ionite in the ammonium form. Experiments showed that curves of the relation of the distribution coefficients for yttrium and cerium between ionite and solution to addend concentration in dioxane-water solutions were similar to curves obtained in aqueous solutions. A series of experiments was carried out with solutions containing 20 and 45% of dioxane at $20 \pm 1^\circ C$. A constant ionic strength of $\mu = 0.2$ was maintained by means of sodium perchlorate. We then measured the distribution coefficient of yttrium and cerium (φ) and addend (α -hydroxyisobutyrate) concentration $\log [A^-] = -2.04$, in relation to the dioxane content of the solution. The data obtained are given in the table. As was to be expected, the separation coefficient of yttrium and cerium (α) increased with a fall in the dielectric constant. On the basis of an experimental relation between φ and the stability constants of complexes MA^{++} [2], an approximate estimate was made of the stability constants of cerium and yttrium α -hydroxyisobutyrate complexes (YA^{++} and CeA^{++} ; A is α -hydroxyisobutyrate) and the values are also given in the table. Irving and Rossotti [3] give an equation for the change in the stability constant of complexes in relation to the mole fraction (n_x) of the organic solvent in solution. By rearranging this equation for the case of complexes of two metals with similar properties (for example, Y and Ce) with the same addend, we obtain an equation of the following type

$$\ln \frac{K_{YA^{++}}}{K_{CeA^{++}}} = A + \frac{n_x}{RT} B + \ln C, \quad (1)$$

where the left-hand part of the equation is the ratio of the stability constants of yttrium and cerium complexes in the mixed solvent, A is the same ratio for pure water, B is a coefficient depending on the change in free energy of the system with a change from the aqueous to the organic phase, and C is the ratio of the activity coefficients,

Distribution Coefficients and Stability Constants of α -Hydroxyisobutyrate Complexes of Yttrium and Cerium in Aqueous Dioxane Solutions

Dioxane content of solution, %	Yttrium		Cerium		$\log \frac{K_{YA^{++}}}{K_{CeA^{++}}}$
	$\log \varphi$	$\log K_{YA^{++}}$	$\log \varphi$	$\log K_{CeA^{++}}$	
0	2.59	3.15	3.65	2.43	0.72
5	2.35	3.30	3.56	2.55	0.75
10	2.15	3.43	3.43	2.62	0.81
20	1.63	3.74	3.14	2.80	0.94
30	1.19	4.00	2.78	3.03	0.97
40	0.59	4.34	2.42	2.35	1.09
50	—	—	2.06	3.47	—
60	—	—	1.79	3.63	—

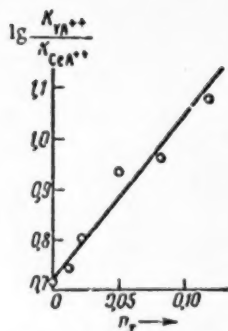


Fig. 1. Relation of the logarithm of the stability constant of the complexes YA^{++} and CeA^{++} to the mole fraction of dioxane in solution (n_x).

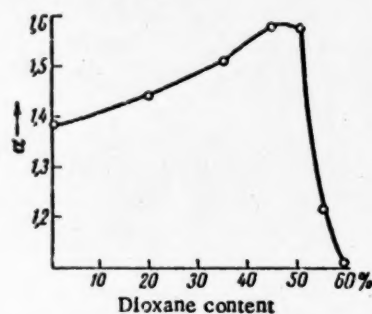


Fig. 2. Change in separation coefficient of promethium and neodymium (α) in relation to the dioxane content of the eluant.

which equals approximately 1 for metals of similar properties. If the coefficient B is linearly dependent on n_x then the equation also becomes linear as occurs in our case (Fig. 1).

From Fig. 1 and also Eq. (1) it follows that the addition of organic solvent substantially increases the separation coefficient of pairs of rare earth elements.

To test this rule under dynamic conditions, we carried out a series of experiments on the chromatographic separation of yttrium, promethium, and neodymium. The separation was carried out on a column 100 mm long, 2.5 mm in diameter, and packed with KRS-200 resin. The eluant was ammonium α -hydroxyisobutyrate, neutralized to pH ~ 5.5 , with various dioxane contents, which was introduced into the column under a small external pressure. Drops of eluate flowing from the column were collected on a continuously moving strip and evaporated under an infrared lamp, and then their activity was measured. A series of experiments was carried out with different concentrations of addend in the eluant and a dioxane content of 0-60% in the solution. With an increase in the dioxane fraction in the solution, there was a considerable change in the surface tension and hence the volume of the drops, and this was considered in comparing the experimental data.

The logarithmic relation of the position of the peak maxima on the elution curves to the addend concentration was linear. As might have been expected from data on separation coefficients obtained under static conditions, with an increase in the dioxane fraction there was also an increase in the degree of separation under dynamic conditions. However, with a strong increase in the dioxane concentration (above 50%) there was again a fall in the separation coefficient, as is shown by Fig. 2. This phenomenon is apparently the result of slowing

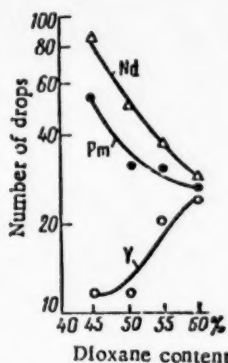


Fig. 3. Reduction of peak maxima of elution curves for Y, Pm, and Nd in relation to the dioxane content of the eluant.

of the motion of the ions, which have a large hydration envelope. It is also reflected in Fig. 3, which gives a semilogarithmic plot of data on the position of the peak maxima of yttrium, promethium, and neodymium elution curves in relation to the dioxane content of the solution. In this case the ammonium α -hydroxyisobutyrate concentration in the eluant was 0.06 M. It will only be possible to explain the observed phenomenon accurately after a more detailed study of the dynamic characteristics of such systems.

Finally, we can conclude that with an increase in the fraction of an organic solvent with low dielectric constant (in the given case, dioxane) there is a strong increase in the stability constant of yttrium and cerium α -hydroxyisobutyrate complexes. At the same time, there is an increase in the separation coefficient in accordance with the linear Eq. (1). An increase in separation coefficient is also observed during chromatographic separation with a maximum at a dioxane content in the eluant of 50%.

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USE OF INFRARED SPECTRA IN THE REGION OF CH VALENCE
VIBRATIONS FOR DETERMINING THE STRUCTURE OF
ALKANES, AROMATIC HYDROCARBONS, AND
COMPOUNDS CONTAINING HETEROATOMS

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In a series of investigations it was shown [1-6] that by measuring the intensity of infrared absorption spectra in the region of C-H valence vibrations ($2800-3000\text{ cm}^{-1}$) it is possible to determine the number of methyl and methylene groups in the molecules of paraffins and thus establish the structure of these compounds. However, for hydrocarbons containing an aromatic ring or heteroatoms (oxygen, sulfur, silicon, or halogen) the solution of this problem is complicated by the effect of these atoms (groups) on the intensities and position of the bands characteristic of CH_2 and CH_3 groups, which lie directly adjacent to them [7-10]. Using a large number of individual compounds, we attempted to determine the limits and possibilities of the application of this method to alkanes with various degrees of branching, mono- and diphenylalkanes, alkyltetralins, alkyl-naphthalenes, normal alcohols, n-alkyl bromides, ketones, and silicohydrocarbons.*

As is known [11], in the region examined the infrared spectra of hydrocarbons show four bands: 2875, 2960, 2856 and 2930 cm^{-1} , of which the first two belong to symmetrical and degenerate vibrations in CH_3 groups, respectively, while the second two belong to symmetrical and unsymmetrical vibrations in CH_2 groups. The band corresponding to methyne groups has a low intensity. It has been found in practice that the most accurate measurements can be made on the intensity of the unsymmetrical vibration bands (2930 and 2960 cm^{-1}), which have a higher intensity than the symmetrical vibration bands and a sharper contour.





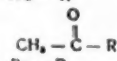
EXPERIMENTAL

Carbon tetrachloride solutions of all the compounds with concentrations no higher than 1-3 g/liter were prepared, and then the infrared spectra were plotted in the region of $2800-3060\text{ cm}^{-1}$ on an IKS-12 spectrometer with a LiF prism in a cell with a constant layer thickness of 1 mm. Apart from making a general record of the bands at 2930 and 2960 cm^{-1} , we measured the intensity at the maximum by the "points" method with the inlet and outlet slits of the spectrometer at a width of about 6 cm^{-1} in this region. As the bands examined overlapped, this complex contour was resolved into components. In the resolution it was assumed that the contours of both bands were symmetrical and could be described by the Lorentz formula $y = A/(x^2 + B)$, where $4B = (\Delta\nu_{1/2})^2$ and $\Delta\nu_{1/2}$ is the half-width of the band $A = BD_{\text{max}}$. This approximation was used previously with success [18, 19]. It was found (see below) that the half-width of the band at 2960 cm^{-1} for most alkanes was 20 cm^{-1} and for the band at 2930 cm^{-1} , 26 cm^{-1} . The same band half-width was found for benzene, naphthalene, and naphthene derivatives. It was somewhat greater for alcohol, tetralins, and alkyl halides. The fact that the half-widths of

*The compounds were synthesized in the Institute of Organic Chemistry, Academy of Sciences USSR and their synthesis is described in [12-17].

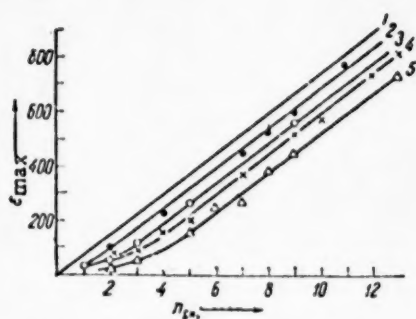
the bands and the distance between these bands in the spectra with $n_{CH_2} > 5$ were constant, generally speaking, made it possible to obtain a calculation formula for determining the degree of overlap of the bands. We then calculated the extinction coefficient (ϵ) from the usual relation: $\epsilon = DM/Cd$ (M is the molecular weight, C is the concentration in g/liter, and d is the layer thickness in cm). The intensity correction allowing for the final width of the instrument slit was not more than 5% under our experimental conditions and was neglected [20]. According to our estimate, the total relative error in the determination of ϵ did not exceed 6%. The results are given in the table, which gives for all the classes of compounds investigated: n_0 , the number of compounds of a given class investigated, $\epsilon_{mean}^{(1)}$ and $\epsilon_{mean}^{(2)}$, coefficients characterizing the absorption of one CH_2 and CH_3 group, respectively ($\epsilon_{mean} = \epsilon/n$, where n is the number of corresponding groups), $\Delta\nu_{1/2}$, the half-width of the corresponding band, and A , the coefficient of the effect (see below).

Characteristics of Infrared Bands of Antisymmetrical CH Vibrations in CH_2 and CH_3 Groups

Type of compound	n_0	CH_2				CH_3	
		$\epsilon_{m}^{(1)}$	$\Delta\nu_{1/2}$	A	Δn	$\epsilon_{m}^{(2)}$	$\Delta\nu_{1/2}$
n-Alkanes	7	75	26	0	0	113	20
Methyl-substituted alkanes	13	75	26	0	0	97	21
"T-shaped" alkanes	10	55	26	100	1,33	132	20
 -R	10	83	26	-40	-0,53	97	21
 -R	17	63	26	60	0,8	100	20
 -R	7	51	26	120	1,6	100	20
 -R	5	51	32	120	1,6	98	20
R_3Si-R	10	53	28	110	1,46	120	19
$\alpha-C_{10}H_7-R$	6	43	26	160	2,13	100	20
$HO-R$	13	43	30	160	2,13	110	20
	9	35	32	200	2,67	120	20
$Br-R$	11	31	32	220	2,94	110	20
$Cl-R$	3	21	30	270	3,6	110	20

DISCUSSION OF RESULTS

Analysis of the experimental material shows that both for normal alkanes [6] and for other types of compound there is a relation between the number of CH_2 groups (n) and $\epsilon_{mean}^{(1)}$, which becomes linear at some value of n (see figure). (For clarity, only some of the curves are given in the figure.) The linear section of each curve may be described by the formula $\epsilon = 75n - A$, where A is a value corresponding to the effect of the groups X ($X = C_6H_5$, OH , R_3Si , halogen, etc.) on adjacent methylene groups of the aliphatic chain R (see table). As the figure shows, this effect of the substituent X on the CH_2 group appears as a reduction in the intensity of the bands of the CH_2 groups with the number of CH_2 groups to which the effect of X extends depending on the nature of X . The greatest effect relative to alkanes ($X = CH_3$, for which $A = 0$) was shown by halogens (A was 200 for Br and 270 for Cl). Since $\epsilon_{mean}^{(1)}$ depends on n ($\epsilon_{mean}^{(1)} = 75 - A/n$) for all classes of compounds where $A \neq 0$, the number of CH_2 groups in the molecule may be determined from the formula $n = \epsilon/75 + \Delta n$, where $\Delta n = A/75$, or graphically. ($\epsilon_{mean}^{(1)}$ was calculated for $n = 5$ in the table.) Δn numerically equals the number of CH_2 groups which are "lost" due to the effect of the substituent X on the intensity of the CH_2 group closest to it. X also affects the intensity of CH_3 group bands. For example, the band of the CH_3 group attached to an aromatic ring in toluene has an intensity of 30 units, in ethylbenzene (in a position β to C_6H_5) 65 units, and then has the value given in the table. The intensity of the CH_3 band in organosilicon compounds changes in almost the same way; for example, in $Si(CH_3)_4$ $\epsilon = 175$ units, i.e., $\epsilon_{mean}^{(2)}$ of one CH_3 group equals approximately 44 units, while for a $\gamma-CH_3$ group in a β -position in respect to Si , $\epsilon_{mean}^{(2)} = 70$ units, in the γ -position 110 units, etc. In alkyl halides the change in intensity of the bands of α -, β -, and $\gamma-CH_3$ groups is even sharper. However, in all cases $\epsilon_{mean}^{(2)}$ is constant for a CH_3 group in the δ -position and then has the value given in the table, so that when $n_{CH_2} > 3$, the number of methyl groups may be determined additionally.

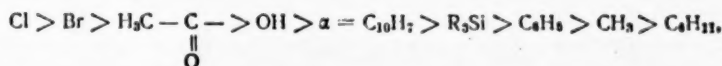


Relation of the intensity of the band at ~ 2930 cm^{-1} to the number of CH_2 groups: 1) *n*-alkanes; 2) $\text{C}_6\text{H}_5\text{—R}$; 3) $(\text{CH}_3)_3\text{Si—R}$; 4) HO—R ; 5) Br—R .

the observed contour of the band attains a half-width of the order of 45 cm^{-1} . This effect is sometimes shown by hydrocarbons with one quaternary carbon atom and leads to some reduction in the mean extinction coefficient for CH_2 groups, though without an appreciable change in $\epsilon_{\text{mean}}^{(1)}$ for CH_2 groups. Monosubstituted cyclohexanes show the opposite effect, namely some increase in $\epsilon_{\text{mean}}^{(1)}$ for CH_2 , and this effect increases additively with compounds with two and more cyclohexyl radicals (with four rings, $A = 160$). In determining the structure of compounds containing several radicals attached to an aromatic ring (but not in the *ortho* positions, where steric factors are substantial), it is necessary to consider the effect of the ring on each of the radicals *R*. Thus, a comparison of the data in the table shows that *A* for disubstituted alkylbenzenes (and biphenyls) is twice as great as for monosubstituted derivatives.

The change in the intensity of CH -vibration bands under the action of the substituent *X* occurs simultaneously with a displacement of the bands (toward long wavelengths when $X = \text{Hal}$ and OH and toward short wavelengths when X is C_6H_5 or $\text{R}_3\text{Si—}$). Therefore, in a short carbon chain (ethyl or propyl) it is not always possible to assign the observed bands unequivocally to CH_2 and CH_3 groups. When the chain contains more than four adjacent methylene groups the bands at 2960 and 2930 cm^{-1} are shown clearly, and their intensity may be determined reliably. This indicates that the given method may be applied to the determination of the structure of hydrocarbons with long aliphatic chains.

In conclusion, it is interesting to note that the value of the coefficient of the effect *A* (table) is qualitatively related to the electronegativity of the group *X*. Thus, if the coefficients *A* are arranged in order of increasing magnitude, we obtain the following series:



which agrees in general with the electronegativity of the groups according to the work of a number of investigators ([21, 22] etc.).

It is interesting that the group R_3Si is more electronegative than phenyl, which agrees with the opinion of some authors [23, 24].

A detailed discussion of this problem is beyond the scope of the present work, but the nature of the gradual extinction of the effect of *X* along the chain and its connection through *A* with the electronegativity of the radical *X* indicates the predominance of the induction effect in the mutual interaction of the radical *X* and adjacent methylene and methyl groups.

As the table shows, the half-widths of the bands at 2930 and 2960 cm^{-1} ($\Delta\nu_{1/2}$) for the types of compound studied change little, and as there is a linear relation between the intensity at the band maximum and the number of CH_2 and CH_3 groups it may be assumed that their integral intensity is a linear function of the number of groups.

Let us consider some details observed in studying the spectra of actual compounds. In a careful repeat study of alkanes (cf. [4]), it was observed that methyl-substituted alkanes (2-methyl-, 3,5-dimethyl-, and 2,4,6-trimethylalkanes and similar compounds) differ very little from *n*-alkanes as regards the characteristics of the intensities of the infrared bands (table), while alkanes with a "T-shaped" molecule (for example, 4-propylheptane and 5-butylnonane) have a coefficient *A* equal to 100, which leads to a "loss" of 1.33 CH_2 groups per branching. With alkanes with two quaternary carbon atoms lying adjacent there is splitting of the band of CH_2 groups at 2960 cm^{-1} , which is not always resolvable by the instrument. Due to this,

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REACTION OF CYCLOHEXENE WITH CONCENTRATED NITRIC ACID

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The nitration of cyclohexene and the mechanism of this reaction have been investigated by a number of authors [1-6, 8-10]. Nitrogen oxides or dilute nitric acid were used as the nitrating agents in this work. The reaction was studied in the liquid phase.

In the present work we investigated the reaction of cyclohexene with highly concentrated (from 98.5 to 99.7% in various experiments) nitric acid in the vapor phase with the ratio of acid to hydrocarbon calculated for complete oxidation (combustion) of the hydrocarbon (5.2:1 by weight). The reaction was carried out at atmospheric pressure in a quartz tube with a diameter of 20 mm at 100° and a contact time of 6.5 sec. Separate experiments were carried out with a contact time of 1.63 sec. It was established that the reaction yielded a complex mixture of products containing in various combinations nitro, nitroso, nitrate, hydroxyl, carbonyl, and carboxyl groups. There is also the possibility that, in accordance with the data of Baldock, Levy, and Scalfe [5], there was also formed a compound containing a nitrite group, namely cyclohexene nitronitrite. The latter could have been hydrolyzed to form nitrocyclohexanol during the treatment. The following reaction products were isolated and identified: cyclohexene pseudonitrosite, nitrocyclohexanone, 1-nitrocyclohexene, ketocyclohexyl nitrate, nitrocyclohexyl nitrate, dinitrocyclohexane, 1,2-cyclohexanedione, a compound with the empirical formula $C_6H_{10}O_2$, 2-nitrocyclohexanol, 1,2-cyclohexanediol mononitrate, adipic acid, oxalic acid, and succinic acid.

It was established that in cases where the compounds isolated could show cis-trans isomerism, a mixture of isomers with the trans-form predominating was usually formed.

Thus, the investigation showed that under the experimental conditions used the reaction of cyclohexene with concentrated nitric acid is a complex reaction in which oxidation processes play a substantial role.

In particular, this investigation is of interest in understanding the spontaneous ignition of cyclohexene with concentrated nitric acid. The accumulation of nitrates (and possibly nitrites) in the preignition period apparently plays a substantial role in this spontaneous ignition. This hypothesis is confirmed by comparing the temperature of spontaneous ignition of cyclohexene with nitric acid and the reaction products isolated and also by the reduction in the so-called "thermal ignition lag" of cyclohexene with nitric acid when nitrates formed in this reaction were preliminarily added to the hydrocarbon.* When investigations of the kinetics of the accumulation of intermediate (in the first instance, unstable) products of this reaction in the preignition period are complete it will be possible to draw more reliable conclusions on the chemistry of the reaction and spontaneous ignition of cyclohexene with nitric acid.

EXPERIMENTAL

The investigation was carried out in a specially designed apparatus. The liquid reaction components, nitric acid (redistilled and containing 0.28-0.3% of nitrogen oxides) and cyclohexene (b. p. 83°, d_4^{20} 0.8107,

*The results of these investigations will be published.

n_D^{20} 1.4470), were passed under pressure from vessels through capillaries to evaporators. The required ratio between them was maintained by having an appropriate pressure drop in the capillaries. The nitric acid and cyclohexene vapors were passed from the evaporators through coils maintained at 100° into a mixer and then into the reaction tube whose length provided for the required contact time. The reaction products were condensed in four successive traps cooled with liquid nitrogen. The reaction mixture was treated with iced water, and the dark green oily product which settled to the bottom was separated from the aqueous layer, washed several times with cold water, and dissolved in ether. When cyclohexene pseudonitrosite was formed in the reaction, crystals were deposited from the ether solution. After the crystals had been collected, the ether solution was neutralized with 10% sodium bicarbonate solution, then washed with water and dried with magnesium sulfate. The ether was removed and the dry oil vacuum distilled into narrow fractions. A small amount of solution was taken from the aqueous layer for isolation of the dibasic acids. The remaining aqueous layer was neutralized with dry sodium bicarbonate with cooling and repeatedly extracted with ether. The extracted products were vacuum distilled to give narrow fractions. The aqueous layer after separation of the neutral products was acidified for extraction of the acids.

Cyclohexene pseudonitrosite was precipitated from the ether solution of the oily reaction product (see above). It was isolated in experiments with a contact time of 1.63 sec (48 g from 830 g of starting cyclohexene). Three recrystallizations from ethyl acetate gave crystals with m. p. 145-145.5°. A mixture with synthetic cyclohexene pseudonitrosite melted at 146°.

Nitrocyclohexanone* was isolated from a fraction of the oily layer with b. p. 54-60° at < 1 mm (after separation of the crystals which precipitated previously) as a flocculent precipitate (0.09 g), which deliquesced in air to give a viscous, dark brown mass. The precipitate formed when an ether solution of the fraction was cooled to -20°. The product was identified by preparation of the phenylhydrazone, which melted at 125.5-128.5° after three recrystallizations from alcohol.

Found %: C 61.86, 61.80; H 6.64, 6.66; N 18.72, 18.77. $C_{12}H_{15}N_3O_2$. Calculated %: C 61.8; H 6.43; N 18.02.

It was also identified by comparing the infrared spectrum of the phenylhydrazone with literature data [7].

1-Nitrocyclohexene was identified in the fraction of the oily layer with b. p. 60-64° at < 1 mm (9 g); n_D^{20} 1.5055, d_4^{20} 1.1354; MR_D 33.2 (calculated 32.86); it decolorized bromine in carbon tetrachloride solution.

Found %: C 56.59, 56.63; H 7.04, 7.08; N 11.0, 10.88. $C_6H_9O_2N$. Calculated %: C 56.7; H 7.1; N 11.02.

Infrared spectral analysis data showed that 1-nitrocyclohexene was also present in other fractions of the oily layer (11.62 g): a) in fractions with b. p. 74-76° and 80-82° at 1 mm (in a predominating amount together with ketocyclohexyl nitrate and nitrocyclohexanol); b) in fractions with b. p. 87-90°, 90-94°, and 95-96°, at < 1 mm (together with ketocyclohexyl nitrate, with the amount of the latter increasing with a rise in the boiling point of the fraction).

Ketocyclohexyl nitrate was isolated as crystals from the fraction of the oily layer with b. p. 97-99° at 1 mm (18.36 g) when the latter was cooled with dry ice. The product was recrystallized from ligroin. It had m. p. 31.5-32.2°.

Found %: C 45.69, 45.79; H 5.68, 5.69; N 8.91, 8.86. $C_6H_9NO_4$. Calculated %: C 45.28; H 5.66; N 8.88.

The 2,4-dinitrophenylhydrazone of ketocyclohexyl nitrate melted at 118-119°.

Found %: C 43.12, 43.10; H 3.95, 4.19; N 21.99, 21.54. $C_{12}H_{13}O_7N_5$. Calculated %: C 42.5; H 3.83; N 20.6.

According to infrared spectral analysis data, ketocyclohexyl nitrate was also present in fractions boiling at higher temperatures (up to the fraction with b. p. 107-110° at 1 mm: 22.6 g).

Nitrocyclohexyl nitrate constituted the fraction of the oily layer with b. p. 123-125° at 1 mm (1.72 g), n_D^{20} 1.4932, d_4^{20} 1.3342; MR_D 41.39 (calculated 41.46); molecular weight 182 (calculated 190).

*The results for a reaction with a contact time of 6.5 sec are given here and later. A total of 3192 g of nitric acid and 614 g of cyclohexene were consumed.

Found %: C 37.77, 37.80; H 5.37, 5.14; N 14.68, 14.44. $C_6H_{10}N_2O_5$. Calculated %: C 37.9; H 5.26; N 14.73.

It was also identified by comparing the infrared absorption spectrum with that of a synthetic product and literature data [7]. According to infrared spectral analysis data, fractions with boiling points of 112 to 122° at 1 mm (18 g) contained considerable amounts of nitrocyclohexyl nitrate and also a small amount of ketocyclohexyl nitrate.

Dinitrocyclohexane was present in the fraction of the oily layer with b. p. 110-115° at < 1 mm (2.53 g), n_D^{20} 1.4929, d_4^{20} 1.3260; MR_D 38.12 (calculated 38.45).

Found %: C 40.94, 40.95; H 5.48, 5.41; N 15.9, 16.1. $C_6H_{10}N_2O_4$. Calculated %: C 41.4; H 5.7; N 16.0.

1,2-Cyclohexanedione was isolated when the reaction was carried out under conditions that differed slightly from those described above. In particular, the nitric acid and cyclohexene vapors were introduced into the mixture at 90° and the cyclohexene consumption at the end of the reaction was higher. The compound was present in the oily layer with b. p. 53-54° at < 1 mm, n_D^{20} 1.5065, d_4^{20} 1.1305.

Found %: C 64.23, 64.28; H 7.11, 7.13. $C_6H_8O_2$. Calculated %: C 64.28; H 7.14.

After recrystallization from alcohol, the phenylhydrazone of the diketone obtained melted at 149.5-150.5°. A mixture with the phenylhydrazone of authentic 1,2-cyclohexanedione melted at 150-151°.

Found %: C 74.10, 73.93; H 6.88, 6.74; N 18.31, 18.46. $C_{18}H_{20}N_4$. Calculated %: C 74.00; H 6.85; N 19.15.

The product with the empirical formula $C_6H_{10}O_2$ precipitated as white crystals (3.03 g) from fractions from the aqueous layer with b. p. 50-90° and 46-48° at 1 mm when they were cooled to 0 to 5°. After recrystallization from ethyl acetate, the substance melted at 136-137°.

Found %: C 62.76, 62.65; H 9.04, 8.9.

Treatment of the product with 1 N aqueous NaOH solution for 26 hr at room temperature yielded (on acidification) adipic acid. The structure of this compound is being established at the present time.

2-Nitrocyclohexanol was isolated as crystals from a fraction from the aqueous layer with b. p. 88-90° at < 1 mm (4.75 g) when it was cooled to 0 to 5°, and after recrystallization from ligroin the product had m. p. 46-47.2°. The melting point of a mixture with synthetic 2-nitrocyclohexanol was 46.5-47.5°. The derivative obtained with 3,5-dinitrobenzoyl chloride melted at 145-146°. A mixed melting point with the derivative of synthetic 2-nitrocyclohexanol was not depressed.

Found %: N 12.32, 12.48. $C_{12}H_{13}N_3O_5$. Calculated %: N 12.39.

According to infrared spectral analysis data, 2-nitrocyclohexanol was also present as a mixture with 1,2-cyclohexanediol mononitrate in fractions with b. p. up to 97° at < 1 mm (a total of 7.4 g).

1,2-Cyclohexanediol mononitrate was identified from the infrared absorption spectrum in fractions from the aqueous layer with b. p. 88-90° and 91-94° at < 1 mm by comparison with the spectrum of synthetic 1,2-cyclohexanediol mononitrate and data given by Brown [7].

Adipic acid was isolated from the ether extract from the acidified aqueous layer. After three sublimations, the acid melted at 150-150.8°. The melting point of a mixture with pure adipic acid was 150-150.7°.

Oxalic acid was isolated from the mixture of dibasic acids remaining after evaporation of a sample of the aqueous layer (see above). The dry residue was dissolved in water. The acid was precipitated as the calcium salt by the addition of a saturated solution of calcium chloride. The precipitated salt was washed several times with hot water and decomposed with 30% HCl. The oxalic acid was isolated from the aqueous solution by repeated extraction with ether. After three sublimations, the acid melted at 186°. The melting point of a mixture with pure oxalic acid was 186-187°.

Found %: C 26.61, 26.73; H 2.22, 2.23. $C_2H_2O_3$. Calculated %: C 26.67; H 2.23.

Succinic acid was detected qualitatively in the mixture of dibasic acids by an intense yellow-green fluorescence (formation of succinyl fluorescein).

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SYNTHESIS AND THERMAL STABILITY OF THE DIHYDRATES OF ZIRCONIUM AND HAFNIUM OXYNITRATES

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Zirconium and hafnium nitrates are acquiring increasing importance in the technology of these elements, especially with the development of extraction methods for separation. However, there are very inadequate and contradictory data in the literature on the composition and properties of zirconium nitrates; hafnium nitrates have not been described at all.

Zirconium oxynitrates are normally prepared by evaporation of nitrate solutions [1-6]. Depending on the evaporation temperature, compounds of various compositions may be formed [3-5, 7, 8]: $3\text{ZrO}_2 \cdot 2\text{N}_2\text{O}_5$, $\text{ZrO}_2 \cdot \text{N}_2\text{O}_5$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{ZrO}(\text{NO}_3)_2 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, $\text{ZrO}(\text{OH})\text{NO}_3$, $\text{ZrO}(\text{OH})\text{NO}_3 \cdot 2\text{H}_2\text{O}$. In the opinion of many authors [9] these oxynitrates are the products of definite stages of the hydrolysis of normal zirconium nitrate. Depending on the experimental conditions (nitric acid and zirconium concentrations and evaporation temperature), it is possible to obtain zirconium and hafnium oxynitrates of various composition. Zirconyl nitrate dihydrate $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, which is a white crystalline substance that dissolves readily in water, is formed by keeping a nitric acid solution of zirconium hydroxide over concentrated H_2SO_4 [6], or by evaporation of the solution at 65° [5]. Raising the temperature to 100° leads to the formation of a vitreous mass, whose composition corresponds to the formula $\text{ZrO}(\text{OH})\text{NO}_3$. During the thermal decomposition of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ there is also the formation of oxynitrates of various compositions [8]: $3\text{ZrO}(\text{NO}_3)_2 \cdot \text{ZrO}_2 \cdot 7\text{H}_2\text{O}$ (110°), $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{ZrO}_2 \cdot 4\text{H}_2\text{O}$ (150°), $\text{ZrO}(\text{NO}_3)_2 \cdot 7\text{ZrO}_2 \cdot 5\text{H}_2\text{O}$ (215°), $\text{ZrO}(\text{NO}_3)_2 \cdot 10\text{ZrO}_2 \cdot 4\text{H}_2\text{O}$ (250°), and ZrO_2 is formed only above 250° . Zirconium oxynitrates in which the Zr: HNO_3 ratio is less than 1:1 are sparingly soluble in water, and their aqueous solutions are strongly opalescent. It should be mentioned that zirconyl nitrate dihydrate is obtained most simply. However, most methods for preparing it are difficult to reproduce, and the composition of the preparation usually corresponds to the approximate formula $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, though considerable amounts of other basic nitrates which are difficultly soluble in water are sometimes present. Therefore, it seemed interesting to search for reproducible methods for synthesizing individual zirconium and hafnium nitrates and to study their properties. In the present communication we present the results of investigating the synthesis of dihydrates of zirconium and hafnium oxynitrates and data on their thermal stability.

No individual compound was obtained by slow evaporation of solutions of freshly precipitated hydroxides in concentrated HNO_3 at various temperatures below 100° with varying amounts of HNO_3 . This is probably explained by the fact that freshly precipitated hydroxides contain a very large and variable amount of water, which affects the degree of hydrolysis of the nitrate. Mixtures of various basic zirconium or hafnium nitrates were therefore obtained. Zirconium and hafnium hydroxides dried to constant weight in air were also found to be unsuitable for the synthesis as their solubility in nitric acid of any concentration fell sharply during drying.

In order to avoid these difficulties, we used for the synthesis zirconium (hafnium) oxychloride octahydrate, which contains the anion of a volatile acid and a strictly defined amount of water of crystallization. The starting zirconium and hafnium compounds were spectrally pure and contained only 0.03% of Hf and 2% of Zr,

respectively. A definite weight of the salt was treated with various amounts of 100% HNO_3 ; the weight ratio $\text{MeO}_2 : \text{HNO}_3$ was varied from 1:3 to 1:6. Air was passed through the nitric acid solutions until the yellow color disappeared, and the solutions were then evaporated to dryness on a water bath at 60° with continuous stirring. All the preparations obtained in this way were readily soluble in water and had a constant composition according to chemical analysis data. The results were completely reproducible in many repetitions of the experiments. The optimal ratio of $\text{MeO}_2 : \text{HNO}_3$ may be regarded as 1:45. In this case, the chlorine content of the final product did not exceed 0.006%.

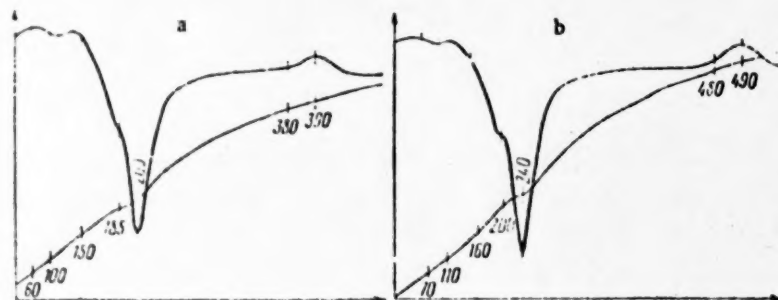


Fig. 1. Thermograms of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (a) and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (b). The mean heating rate was $8-10^\circ/\text{min}$.

The ZrO_2 and HfO_2 contents of the compounds obtained were determined gravimetrically and the N_2O_5 by Devarda's method. The amount of water was calculated from the difference in weight of the substance obtained after firing to constant weight at 900° . The analysis results, which are mean values from 3-4 experiments are given below:

	ZrO_2 , %	HfO_2 , %	N_2O_5 , %	H_2O , %	$\text{MeO}_2 : \text{N}_2\text{O}_5 : \text{H}_2\text{O}$
Hydrated zirconium oxynitrate	46,24	—	39,96	13,80	1 : 0,99 : 2,02
Hydrated hafnium oxynitrate	—	58,98	30,37	10,65	1 : 1,02 : 2,10

In accordance with analysis data, the compounds synthesized should be assigned the formulas: $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

The dihydrates of zirconium and hafnium oxynitrates were white crystalline substances. According to optical analysis data, their crystals were anisotropic. However, the refractive indices were similar, and therefore we were able to determine only their mean values. The measurements were made by the immersion method at 22° . The values of n_{mean} obtained differed very slightly and equalled $1,592 \pm 0,001$ for $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $1,558 \pm 0,001$ for $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. The difference in the density values was also small: the densities were 2,267 and 3,144, respectively, for $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (the densities were determined pycnometrically at $20 \pm 0,1^\circ$).

The conversions undergone by zirconium and hafnium oxynitrates when heated in air were studied by several methods.

The compositions of the residues obtained by firing the compounds to constant weight were determined in the following way. Samples of the salts (0.1-0.5 g) were placed in a drying cupboard ($40-200^\circ$) or a muffle furnace ($250-500^\circ$) heated to a given temperature. Variations in temperature were $\pm 2^\circ$ and $\pm 10^\circ$, respectively. The residues were weighed and analyzed for MeO_2 and N_2O_5 contents. The results of the investigation over the range $40-500^\circ$ are given in Tables 1 and 2.

The equilibrium data obtained show that the zirconium and hafnium compounds differ somewhat in stability and the nature of their decomposition on heating. Dehydration of zirconium oxynitrate dihydrate began even at 40° . Over the range of $40-120^\circ$ there was partial decomposition of the compound, which proceeded slowly without a change in the crystal structure. The slight increase in the percentage water content in the residue is probably explained by the slightly higher rate of removal of N_2O_5 and the high molecular weight of

TABLE 1

Results of Heating $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ to Constant Weight in Air

Temp., °C	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$			$\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$		
	wt. loss %	$\text{ZrO}_2:\text{N}_2\text{O}_5:\text{H}_2\text{O}$ ratio	Residue	wt. loss %	$\text{HfO}_2:\text{N}_2\text{O}_5:\text{H}_2\text{O}$ ratio	Residue
40	1.24	1:0.99:1.83	Crystalline	0.64	1:0.93:2.00	Crystalline
60	1.38	1:0.95:2.20		1.31	1:0.97:1.62	
80	1.66	1:0.93:2.30		2.09	1:0.97:1.65	Crystalline
100	2.46	1:0.92:2.30		4.99	1:0.06:1.00	
120	4.39	1:0.89:2.37	Amorphous to x-rays	5.31	1:1.05:1.00	Crystalline
140	36.88	1:0.30:0.90		23.76	1:0.45:1.3	
160	43.33	1:0.19:0.55		31.40	1:0.28:0.48	Amorphous to x-rays
180	45.15	1:0.18:0.26		35.65	1:0.18:0.56	
200	48.17	1:0.15:0.17	Amorphous to x-rays	35.08	1:0.14:0.48	Amorphous to x-rays
250	52.58	1:0.02:0.20		39.20	1:0.05:0.21	
300	53.16	1:0.01:0.08	Monoclinic ZrO_2	39.50	1:0.01:0.40	Monoclinic HfO_2
400	53.51*	—		40.20*	—	
500	54.37	—		40.70	—	

* Residues obtained after firing $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ at 400° contained traces of N_2O_5 and a small amount of H_2O (0.4-1.0 weight %).

TABLE 2

Results of Analyzing Residues from $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ Obtained by Heating to a Given Temperature at a Rate of 8-10°/min

Compound	Temp., °C	Content, weight %				$\text{MeO}_2:\text{N}_2\text{O}_5:\text{H}_2\text{O}$ ratio
		ZrO_2	HfO_2	N_2O_5	H_2O	
$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	100	46.23	—	39.07	14.70	1:0.96:2.47
	150	70.46	—	25.04	4.50	1:0.40:0.44
	200	82.08	—	14.82	3.10	1:0.21:0.26
$\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	110	—	61.66	32.83	5.51	1:1.03:1.00
	200	—	77.82	19.76	6.39	1:0.50:0.63
	250	—	86.96	10.75	2.29	1:0.24:0.31

N_2O_5 in comparison with H_2O . Over the temperature range 120-200°, the decomposition of zirconium oxynitrate dihydrate proceeded rapidly and was accompanied by disruption of the crystal lattice. At temperatures of 250-400°, the residual small amounts of N_2O_5 (10 weight %) and H_2O (1.5 weight %) were removed and monoclinic ZrO_2 was formed.

The hafnium compound had a higher thermal stability; its decomposition also occurred in stages and these were expressed more clearly. Over the temperature range 60-80°, half a molecule of water was removed; at 100-120°, hafnium oxynitrate monohydrate was stable and an x-ray diffraction pattern of it differed somewhat from that of the dihydrate; above 140°, the decomposition rate increased sharply and the crystal structure of the substance was disrupted. The residues of N_2O_5 and H_2O were removed at 250-300° and monoclinic HfO_2 was formed above 400°.

The heating curves of the compounds, which were plotted with a Kurnakov pyrometer, clearly showed three endothermic and one exothermic effect. The difference in the thermal stability of zirconium and hafnium oxynitrates appeared most clearly in the low-temperature region. The first effect on the thermogram of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (60-100°) was connected with partial decomposition of the compound; the analogous effect (70-100°) for $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ characterized only the removal of the first water molecule as was confirmed by chemical analysis of residues of the compounds (Table 2). The second effect, which was expressed more clearly for $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, covered the temperature ranges of 150-180° and 160-200°, respectively, for zirconium and hafnium and was associated with further dehydration and decomposition of the compounds; according to chemical analysis data, an unstable hafnium oxynitrate with the ratio $\text{HfO}_2:\text{N}_2\text{O}_5 = 2:1$ was formed in this region. The existence of an analogous zirconium compound under the given conditions is less probable. The last endothermic effect characterized the complete decomposition of the zirconium and hafnium compounds and this occurred

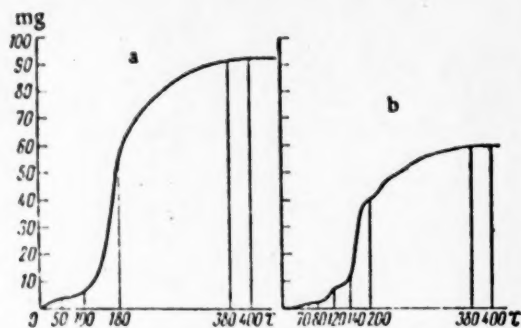


Fig. 2. Curves of weight change during the heating of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (a) and $\text{HfO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (b). The mean heating rate was $5-7^\circ/\text{min}$.

in the temperature ranges of $186-200^\circ$ and $210-240^\circ$, respectively. The exothermic effects were caused by crystallization of monoclinic zirconium and hafnium oxides.

The results of gravimetric analyses completely confirmed the data obtained (Fig. 2). Thus, in the case of the zirconium compound, the change in weight of a sample on heating was expressed by a curve which did not indicate the existence of stable intermediate compounds. A decrease in the weight of the preparation occurred above 40° ; a high decomposition rate was observed over the range of $100-190^\circ$. The process was completed at 400° by the formation of ZrO_2 and in this case the weight loss equalled 54.1%. According to gravimetric analysis data, the decomposition of hafnium oxynitrate dihydrate occurred in stages. One molecule of H_2O was lost over the temperature range of $80-120^\circ$; the formation of dihafnium nitrate was observed in the region of 200° ; and finally, complete decomposition of the compound occurred at $380-400^\circ$.

Thus, the results of the thermal investigation, which were confirmed by x-ray phase and chemical analyses, indicate that zirconium and hafnium oxynitrate dihydrates are thermally unstable compounds and decompose completely at 400° . The decomposition of the hafnium compound proceeds in stages and is accompanied by the formation of the monohydrate and an unstable oxynitrate with an oxide ratio of $\text{HfO}_2 : \text{N}_2\text{O}_5 = 2 : 1$. No monohydrate is formed when $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ is heated and the existence of an intermediate compound is expressed less clearly.

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NEW METHOD OF SYNTHESIZING HYDROXYARYLPHOSPHINIC ACIDS

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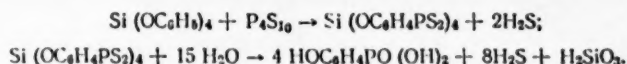
(Presented by Academician S. I. Vol'fkovich, July 19, 1960)

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Hydroxyarylphosphinic acids are obtained from aminoarylphosphinic acids through diazo compounds [1] and by hydrolysis of haloarylphosphinic acids [2] and methoxyarylphosphinic acids [3]. All three methods are based on the replacement of one substituent in the aromatic nucleus of the arylphosphinic acid by a hydroxyl and are not always applicable, and therefore the number of known hydroxyarylphosphinic acids is small. Lecher et al. [4] obtained arylphosphinic acids by phosphorylation of hydrocarbons or alkyl aryl ethers with phosphorus pentasulfide and subsequent hydrolysis of the arylphosphine disulfides obtained. This method is unsuitable for the phosphorylation of phenols as they form arylthiophosphates with phosphorus pentasulfide [5]. In the present work we prepared hydroxyarylphosphinic acids by phosphorylation of phenyl silicate or borate with phosphorus pentasulfide and subsequent hydrolysis according to the scheme:



In practice, phosphorylation did not proceed to completion or there was partial elimination of phosphoric acid during hydrolysis and phenol was obtained, as was pointed out by previous investigators [6]. Nitration of p-hydroxyphenylphosphinic acid yielded picric acid, and analogously, m-cresylphosphinic acid yielded trinitro-m-cresol.

Hydroxyphenyl- and m-cresylphosphinic acids readily formed solid polycondensation products with formaldehyde. On the basis of this and the nitration it is evident that from m-cresol we obtained 1-methyl-3-hydroxybenzene-6-phosphinic acid. The hydroxyarylphosphinic acids underwent azo coupling to form azo dyes.

EXPERIMENTAL

Synthesis of hydroxyphenylphosphinic acid. In a round-bottomed flask with a stirrer, reflux condenser with a calcium chloride tube, and thermometer, 133.2 g (0.3 mole) of phosphorus pentasulfide (technical with m. p. 275-276°) was added to 500 g (1.2 mole) of tetraphenoxysilane, obtained by the method in [7]. The mixture was stirred at 155-170° for 12 hr until the evolution of hydrogen sulfide ceased. On cooling, 500 ml of water was added gradually and the mixture again heated for 20 hr. At the end of hydrolysis (cessation of hydrogen sulfide evolution), the silicic acid was removed by filtration. The phenol layer was separated and the aqueous layer extracted several times with ether and the ether extracts were combined with the phenol layer. When the aqueous layer was evaporated to 1/4 of its volume and cooled, 53.5 g (25.6% of theoretical, calculated on P_4S_{10}) of hydroxyphenylphosphinic acid crystallized from it. After recrystallization from 6 N HCl, the acid had m. p. 173-173.5°.

Found %: C 41.27, 41.27; H 4.11, 4.21; P 17.89, 18.01. $\text{C}_6\text{H}_7\text{O}_4\text{P}$. Calculated %: C 41.39; H 4.05; P 17.79.

Analogously, an equimolecular amount of triphenyl borate yielded 20.8 g of p-hydroxyphenylphosphinic acid (7.5% of theoretical).

Alkali metal salts of p-hydroxyphenylphosphinic acid were readily soluble and Ba, Ca, and Pb salts difficultly soluble in water.

Condensation with formaldehyde. A mixture of 5.1 g (0.3 mole) of p-hydroxyphenylphosphinic acid, 5.3 g of 32% formalin, and 1.5 ml of a 25% aqueous solution of ammonia was heated on a bath for 1.5 hr and then the resin precipitated. It was washed with water and dried at 150° for 3 hr. We obtained 6.2 g of a solid orange resin containing P, C, and H, which did not change up to 300° and was insoluble in water and the usual solvents.

Synthesis of o-cresylphosphinic acid. As above, from 392 g (0.86 mole) of tetra-o-cresyl silicate, obtained by a method in [8], and 89 g (0.2 mole) of phosphorus pentasulfide we obtained 53 g of cresylphosphinic acid. The acid was partly soluble in ether and o-cresol. For its extraction, an ether solution of the o-cresol was extracted several times with 3% sodium carbonate solution; the alkaline extracts were acidified with hydrochloric acid and extracted with ether, and the ether removed to yield a further 7.2 g of o-cresylphosphinic acid, giving a total of 60.2 g (40% on P_4S_{10}). The product was purified by recrystallization from 6 N HCl and had m. p. 160°.

Found %: C 44.33, 44.32; H 5.47, 5.04; P 15.28, 16.15. $C_7H_9O_4P$. Calculated %: C 44.69; H 4.82; P 16.46.

o-Cresylphosphinic acid was readily soluble in water, alcohol, and acetone and less so in ether. It was insoluble in benzene and ligroin; the Li, Na, and K salts were readily soluble in water, while the Ca, Ba, and Pb salts were difficultly soluble.

Synthesis of p-cresylphosphinic acid. The reaction was analogous to the synthesis of o-cresylphosphinic acid. The yield was 30 g (20%, calculated on P_4S_{10}). The product was recrystallized from 6 N HCl and had m. p. 218°.

Found %: C 45.22, 45.15; H 4.55, 4.51; P 16.18, 16.19. $C_7H_9O_4P$. Calculated %: C 44.69; H 4.82; P 16.46.

The acid was readily soluble in water, alcohol, and acetone, difficultly soluble in ether, and insoluble in benzene; the Li, Na, and K salts were readily soluble and the Ba and Pb salts insoluble in water.

Synthesis of m-cresylphosphinic acid. The reaction was analogous to that above. We obtained 11.5 g of sirupy m-cresylphosphinic acid (about 30%). On standing for 20 days in a desiccator, the product crystallized.

Synthesis of an azo dye with p-diazonitrobenzene. To a solution of 1.5 g of m-cresylphosphinic acid in 20 ml of 2% sodium hydroxide was added ice and the acid coupled with a diazo solution from 1.4 g of p-nitroaniline. Coupling occurred in 6 hr. We obtained 1.75 g of an orange dye. It was recrystallized from alcohol.

Found %: N 9.4, 9.45; P 12.2, 12.32. $C_{13}H_{12}O_6N_2P$. Calculated %: N 12.5; P 9.22.

Condensation with formaldehyde. From 4 g of p-cresylphosphinic acid we obtained 6.3 g of resin analogously to the synthesis from p-hydroxyphenylphosphinic acid.

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ORGANOBORON COMPOUNDS

COMPLEX COMPOUNDS OF BORANE AND PHENYLBORANE WITH DIETHYLAMINE AND SOME OF THEIR CONVERSIONS

B. M. Mikhailov and V. A. Dorokhov

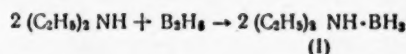
N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
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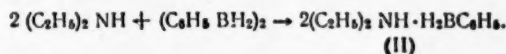
By the reaction of dimethylamine and diborane, Wiberg et al. [1] obtained dimethylaminoborane, which was converted into bis-(dimethylamino)-diborane by heating. By the action of diethylamine on diborane, the same authors obtained a colorless solid and they assigned it the structure of diethylamineborane [1]. Burg and Good recently synthesized a series of complex compounds of borane with cyclic secondary amines and converted them into the corresponding aminoboranes [2].

By investigating the reaction between diethylamine and diborane in ether, we found that it gives a 90% yield of diethylamineborane (I).



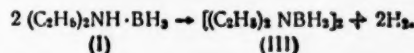
Contrary to the data of Wiberg et al. [1], it is not a crystalline substance, but distills in vacuum as a colorless liquid, which is resistant to water and alcohols at room temperature.

1,2-Diphenyldiborane behaved analogously toward diethylamine and was converted smoothly into diethylaminephenylborane (II), which was much less stable thermally than I.



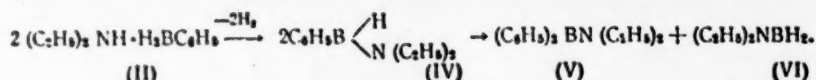
Determination of the molecular weight of the compounds I and II obtained by the cryoscopic method showed that they are associated in benzene. It is probable that these compounds are associated to an even greater extent in the liquid form as is indicated by the comparatively high boiling point of diethylamineborane (I).

At 130-150°, diethylamineborane (I) lost hydrogen and was converted smoothly into bis-(diethylamino)-borane (III), which is a crystalline substance, subliming in vacuum.



III hardly reacted with water and alcohols at room temperature, but reacted at an appreciable rate above 60°.

When heated in vacuum (at 90-150°), diethylaminephenylborane lost hydrogen and was converted into a mixture of diphenyldiethylaminoboron (V) and diethylaminoborane (VI).



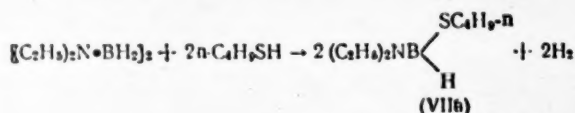
Diethylaminoborane (VI) was collected in a trap at -70° as a mobile liquid, which dimerized with the evolution of heat when the temperature was raised and formed crystalline bis-(diethylamino)-diborane (III).

Phenyldiethylaminoborane (IV) was evidently formed in the first stage of the pyrolysis and this then symmetrized to (V) and (VI). The symmetrization was reversible, and when the VI was removed from the reaction sphere the equilibrium $\text{IV} \rightleftharpoons \text{V} + \text{VI}$ was displaced completely to the right.

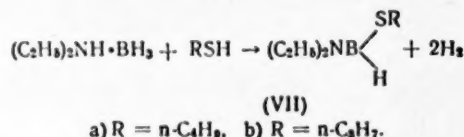
Pyrolysis of II at atmospheric pressure yielded, in addition to diphenyldiethylaminoborane (V), a fraction which reacted vigorously with alcohol with the evolution of hydrogen. The same fraction was obtained by heating V and VI. According to analysis data, the fraction was IV, probably with a trace of III, from which it could not be freed completely by distillation.

It is interesting that Burg and Boone investigated the disproportionation of methyldiethylaminoborane to dimethyl-(diethylamino)-boron and dimethylaminoborane and found that the process is of an equilibrium nature [3].

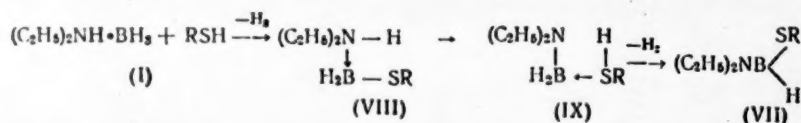
Bis-(diethylamino)-diborane reacted with n-butyl mercaptan at 100° to form n-butylmercapto-(diethylamino)-borane, which is a new type of substituted borane.



Alkylmercapto-(diethylamino)-boranes (VII) may be obtained in 85% yield by the direct action of mercaptans on diethylaminoborane at 100° .

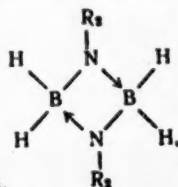


The process apparently proceeds according to the following scheme:



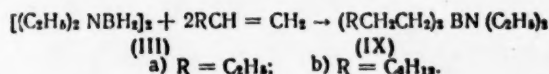
In accordance with this, a complex of diethylamine and the alkylmercaptoborane (VIII) is formed in the first stage of the reaction with the evolution of hydrogen and this complex is converted into a complex of diethylaminoborane with the mercaptan (IX). The latter loses hydrogen and is converted to VII.

Alkylmercapto-(diethylamino)-boranes (VII) are unpleasant-smelling liquids, which are oxidized rapidly in air and distill in vacuum without decomposition. They exist in a monomeric form and this is responsible for their capacity to react vigorously with alcohols with the liberation of hydrogen, as in the case of phenyldiethylaminoborane. On the other hand, dimeric derivatives of borane with dialkylamino groups such as bis-(dialkylamino)-diboranes, which have the structure



are inert toward alcohols at room temperature.

Bis-(diethylamino)-diborane (III) added to olefins at 120-130° in the presence of pyridine. In this way we obtained di-n-butyl-diethylaminoboron (IXa) and di-n-octyl-diethylaminoboron (IXb).



The addition of III to olefins proceeds with even greater difficulty and gives lower yields than the addition of tetraalkylmercaptodiboranes [4].

EXPERIMENTAL

All operations were carried out in an atmosphere of dry nitrogen. Diborane was obtained by the action of boron trifluoride etherate on sodium borohydride in ether in 60-70% yield.

Diethylamineborane (I). Into a stirred solution of 18.2 g (0.25 mole) of diethylamine in 70 ml of absolute ether was passed 0.14 mole of diborane over a period of 5 hr. The ether was then removed in vacuum and the residue distilled. We obtained 20.1 g of diethylamineborane (92%) with b. p. 75-77° at 2.5 mm, m. p. -24 to -20°, d_4^{20} 0.7568, n_D^{20} 1.4358.

Found %: C 55.74; H 16.22; B 12.62. C₄H₁₄BN. Calculated %: C 55.24; H 16.10; B 12.44.

Molecular weight found: 116.9; calculated 87.0.

Bis-(diethylamino)-diborane (III). Into a flask fitted with a reflux condenser and connected to a gasometer was placed 13.9 g (0.16 mole) of diethylamineborane and the compound heated on an oil bath at 130-150° for 7 hr. During this time, 3300 ml of hydrogen was liberated. The reaction product (13.0 g) crystallized on cooling. Purification by vacuum sublimation yielded 12.1 g (89%) of bis-(diethylamino)-diborane with m. p. 42-44°.

Found %: C 56.65; H 14.14; B 12.23. C₈H₂₄N₂B₂. Calculated %: C 56.54; H 14.24; B 12.73.

Molecular weight found: 159.1, 164.1; calculated 169.9.

Diethylaminephenylborane (II). A solution of 5.1 g (0.07 mole) of diethylamine in 18 ml of absolute ether was added dropwise to a solution of 5.4 g (0.03 mole) of 1,2-diphenyldiborane [5] in 90 ml of absolute ether, cooled to -30°. The ether was then removed in vacuum and the residue kept in vacuum (2 mm Hg) until it reached constant weight (about 30 min). We obtained 9.75 g of diethylaminephenylborane as a viscous liquid with n_D^{20} 1.5290. The yield was almost quantitative.

Found %: C 73.68; H 10.55; B 7.12. C₁₀H₁₈BN₂. Calculated %: C 73.62; H 11.12; B 6.63.

Molecular weight found: 184.5, 190.4; calculated 163.

Pyrolysis of diethylaminephenylborane. a) Into a flask connected to a reflux condenser and a trap cooled to -70° was placed 9.6 g (0.06 mole) of diethylaminephenylborane and the compound heated in vacuum on an oil bath (80-110°) for 2.5 hr. In the trap there collected 2.2 g of a liquid, which rapidly crystallized with strong heat evolution when heated to room temperature. The crystalline substance formed was bis-(diethylamino)-diborane (88% yield) with m. p. 41-44°.

Found %: B 12.00. C₈H₂₄N₂B₂. Calculated %: B 12.73.

The residue in the reaction flask was fractionally distilled to yield 5.6 g (80%) of diphenyldiethylaminoboron with b. p. 128-132° at 2.5 mm and m. p. 38-39.5°. Literature data: m. p. 36-37° [6].

Found %: B 4.58. C₁₆H₂₀BN. Calculated %: B 4.60.

b) A 10.9-g sample (0.067 mole) of diethylaminephenylboron was heated at 90-150° in a flask connected to a gasometer. We collected 1400 ml of hydrogen. The reaction products were subjected to fractional distillation. We isolated a fraction with b. p. 58-63° at 2.5 mm (4.9 g) and a fraction with b. p. 125-123° at 2.5 mm (4.0 g). After redistillation, the first fraction had b. p. 48-50° at 1.5 mm, n_D^{20} 1.5015. It reacted vigorously with alcohol, liberating hydrogen.

Found %: C 73.00; H 10.33; B 7.62.

The second fraction crystallized in the receiver and was diphenyldiethylaminoboron with m. p. 38-39.5°.

n-Butylmercapto-(diethylamino)-borane (VIIa). a) A mixture of 6.1 g (0.036 mole) of bis-(diethylamino)-diborane and 6.8 g (0.075 mole) of n-butyl mercaptan was heated at 90-110° for 2 hr. We collected 1550 ml of hydrogen. Distillation yielded 10.6 g (85%) of n-butylmercapto-(diethylamino)-borane with b. p. 49-51° at 1.5 mm, d_4^{20} 0.849, n_D^{20} 1.4636.

Found %: C 55.67; H 11.72; B 6.43; S 18.50. $C_8H_{19}BNS$. Calculated %: C 55.52; H 11.65; B 6.25; S 18.52.

Molecular weight found: 176.3, 172.2; calculated 173.1.

b) A mixture of 10.2 g (0.117 mole) of diethylamineborane and 11.3 g (0.125 mole) of n-butyl mercaptan was heated at 110-120° for 1.5 hr. We collected 5200 ml of hydrogen. Distillation yielded 17.5 g of n-butylmercapto-(diethylamino)-borane with b. p. 49-51° at 1.5 mm. The yield was 86%.

n-Propylmercapto-(diethylamino)-borane (VIIb). A mixture of 7.7 g (0.088 mole) of diethylamineborane and 7.0 g (0.092 mole) of n-propyl mercaptan was heated at 80-120° for 3.5 hr. During the heating, 3900 ml of hydrogen was liberated. Distillation yielded 11.6 g (82%) of n-propylmercapto-(diethylamino)-borane with b. p. 79-81° at 17 mm, d_4^{20} 0.848, n_D^{20} 1.4628.

Found %: C 52.52; H 11.50; B 7.08; S 19.89. $C_7H_{16}BNS$. Calculated %: C 52.84; H 11.40; B 6.80; S 20.15.

Molecular weight found: 166.5; calculated 159.1.

Addition of bis-(diethylamino)diborane to butene. Into a flask fitted with a thermometer and reflux condenser were placed 7.1 g (0.042 mole) of bis-(diethylamino)-diborane and 0.4 ml of pyridine. Butene was passed into the mixture at 120-130° for 10 hr. Fractional distillation yielded 7.8 g (48%) of dibutyldiethylaminoboron with b. p. 52-55° at 1.5 mm, d_4^{20} 0.781, n_D^{20} 1.4377.

Found %: C 73.50; H 14.55; B 5.45. Calculated %: C 73.10; H 14.30; B 5.48.

In the experiment we also obtained a low-boiling fraction, containing a substance which reacted with alcohol with the liberation of hydrogen. This fraction was not investigated more thoroughly.

Addition of bis-(diethylamino)-diborane to octene. A mixture of 4.0 g (0.024 mole) of bis-(diethylamino)-diborane, 10.8 g (0.096 mole) of 1-octene, and 0.3 ml of pyridine was heated at 110-130° for 4 hr. Fractional distillation yielded 4.3 g (30%) of dioctyldiethylaminoboron with b. p. 150-152° at 2 mm, d_4^{20} 0.8072, n_D^{20} 1.4502.

Found %: C 78.04; H 14.32; B 3.46. Calculated %: C 77.62; H 14.33; B 3.50.

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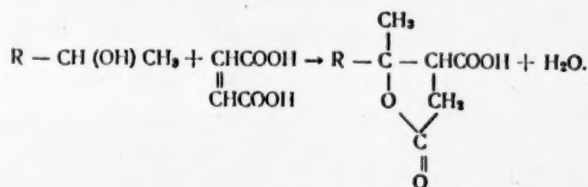
FREE-RADICAL ADDITION OF ALCOHOLS TO ACRYLIC ACID AND ITS METHYL ESTER

SYNTHESIS OF γ -LACTONES

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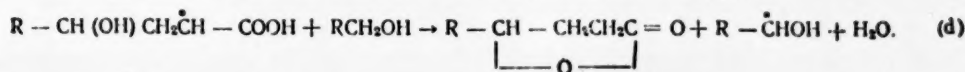
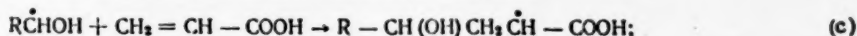
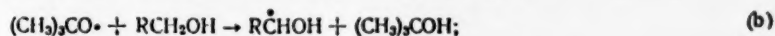
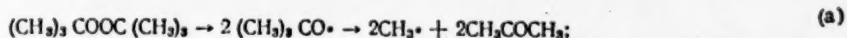
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Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 2, pp. 360-363,
January, 1961
Original article submitted September 13, 1960

Many natural organic compounds containing a γ -lactone grouping have a strong physiological action on micro- and macroorganisms, while alkyl γ -lactones have valuable perfume properties. In a series of papers [1-3] it was shown that γ -lactones (γ -alkylparaconic acids) may be obtained by the reaction of isopropanol, 2-octanol, and ethanol with maleic acid.



The reaction was carried out in the presence of benzophenone with prolonged (18-25 hr) irradiation with ultraviolet light and the lactone yields were 18-38% in most cases.

In the present work we studied the addition of alcohols to acrylic acid and its methyl ester with tert-butyl peroxide as the initiator. It was established that γ -lactones are formed with both acrylic acid and methyl acrylate. The reaction of acrylic acid with alcohols proceeds by a free-radical chain mechanism, which may be represented by the following series of equations:



The abstraction of a hydrogen atom from an alcohol molecule may also be effected by a methyl radical. The reaction with methyl acrylate proceeds analogously. In this case, methyl esters of γ -hydroxy acids evidently

are formed initially, and these are then converted to γ -lactones as a result of intramolecular transesterification. The conditions of individual experiments, amounts of reaction components and peroxides, yields of 1:1 adducts, and amounts of high-boiling products formed are given in Table 1. Table 3 gives the properties of the lactones obtained.

TABLE 1

Expt. No.	Reactants		Amounts of reactants, mole			Temp., °C	Time, hr	Yield of 1:1 adduct		Residue, g
	A	B	A	B	peroxide			g	%	
1	1-Heptanol	Acrylic acid	3	0.3	0.045	160-170	6.5	36	70.5	21
2	1-Heptanol	Methyl acrylate	3	0.3	0.045	160-170	6.5	36.5	71.5	17.4
3	2-Octanol	Acrylic acid	3	0.3	0.045	160-170	6.5	33.5	60.6	18.8
4	2-Ethyl-1-hexanol	Acrylic acid	2.6	0.26	0.039	160-170	6	19.8	41.5	25
5	Cyclohexanol	Acrylic acid	3	0.3	0.045	156-163	6.5	40	86.5	3.2
6	Benzyl alcohol	Acrylic acid	3	0.3	0.045	160-170	6	27	56	21
7	1-Nonanol	Methyl acrylate	3	0.15	0.075	155-165	3	26	87	17.4

TABLE 2

Reaction of 1-Nonanol (A) with Acrylic Acid (B)

Expt. No.	Amt. of reactants, mole			Temp., °C	Time, hr	Yield of 1:1 adduct		Residue, %
	A	B	peroxide			g	%	
8	3	0.3	0.09	160-170	6.5	43	72.3	20.5
9	3	0.3	0.045	160-170	6.5	38.8	65	20
10	3	0.3	0.0225	160-170	6.5	26.5	45	29.5
11	3	0.3	0.0075	160-170	6.5	15	25	40

We studied the reaction of acrylic acid with heptanol, nonanol, sec-octanol, 2-ethylhexanol, cyclohexanol, benzyl alcohol, and γ -phenylpropanol (experiment Nos. 1, 3-6, and 8-11) and the reaction of methyl acrylate with heptanol and nonanol (experiment Nos. 2 and 7). Only in the case of γ -phenylpropanol was it impossible to obtain a lactone, and only high-molecular polymerization and telomerization products, which were not investigated, were formed. With the other alcohols, γ -lactones were obtained in quite high yields with a molar ratio of alcohol: acid: peroxide of 10:1:0.15. The comparatively low yield (41.5%) of the lactone from 2-ethylhexanol is evidently explained by the ease of abstraction of a hydrogen atom from the tertiary carbon atom of this alcohol and the low reactivity of the free radical formed, which tends to dimerize and disproportionate. Even with benzyl alcohol, it was possible to obtain γ -phenylbutyrolactone in 56% yield despite the fact that benzyl radicals have a low reactivity [4].

In order to study the effect of the amount of peroxide on the yield of γ -octylbutyrolactone, we carried out a series of experiments with various molar ratios of 1-nonanol: acrylic acid: peroxide (Table 2). The properties of the lactone obtained are given in Table 3. The figure gives a graphical representation of the relation of lactone yield, calculated on peroxide and acrylic acid, to the amount of tert-butyl peroxide.

When the reaction of nonanol with acrylic acid was initiated with benzoyl peroxide, γ -octylbutyrolactone was obtained in an insignificant yield.

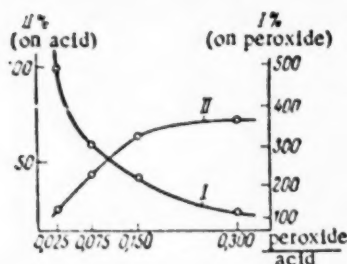
TABLE 3

Expt. No.	γ -Lactone (1:1 adduct)	Molecular weight		B.p., °C (mm Hg)	d_4^{20}	n_D^{20}	MRD		Elementary analysis			
		found ^d	calcd.				found	calcd.	found, %		calculated, %	
									C	H	C	H
1 ^a	$C_4H_9CH-CH_2CH_2C=O$	166.9	170.25	97—100(1)	0.9482	1.4482	48.09	48.07	—	—	—	—
2	$C_4H_9CH-CH_2CH_2C=O$			95—97(1)	0.9478	1.4485	48.13	48.07	70.61	10.71	70.56	10.66
3	$(C_4H_9)(CH_2C-CH_2CH_2C=O)$	183.6	184.28	97—98(1)	0.9433	1.4496	52.46	52.72	70.60	10.76	71.73	10.80
4	$C_4H_9-CH-CH-CH_2CH_2C=O$	185.1	184.28	100—101(1)	0.9488	1.4545	52.65	52.72	71.53	10.91	71.69	10.94
5	$(CH_3)_2C-CH_2CH_2C=O$	152.3	154.21	90—92(1.5)	1.0735	1.4817	40.93	41.53	70.20	9.25	70.09	9.15
6 ^a	$C_4H_9CH-CH_2CH_2C=O$			125—127(1.5)	—	—	—	—	70.34	9.15	74.24	6.21
7 ^a	$C_4H_9CH-CH_2CH_2C=O$	162.0	162.19	130—132(1.5)	0.9342	1.4521	57.27	57.37	74.16	6.13	74.06	—
9	$C_4H_9CH-CH_2CH_2C=O$	195.4	198.30	120—121(1)	0.9334	1.4520	57.32	57.37	72.96	11.26	72.60	11.18

^a The molecular weight was determined from the ester number.

^b M. P. 36.5-37° (from acetone and from heptane).

^c Literature data: experiment No. 1, b. p. 281° [5]; No. 6, m. p. 37° [6]; b. p. 130-130.3° (1.5 mm), m. p. 45.5-46° [7]; No. 7, b. p. 130° (0.5 mm), d_4^{20} 0.9383, n_D^{20} 1.4522 [8].



Yield of γ -octylbutyrolactone, calculated on peroxide and acid, in relation to the molar ratio of peroxide: acrylic acid. The molar ratio 1-nonanol: acrylic acid = 10:1, the reaction temperature was 160-170°, and the reaction time 6.5 hr.

EXPERIMENTAL

All experiments given in Tables 1 and 2 were carried out by the same procedure. A solution of the calculated amounts of acrylic acid (or its methyl ester) and tert-butyl peroxide was prepared in part of the alcohol taken from the total calculated amount given in Tables 1 and 2. For preparing these solutions we used 1.3 mole of alcohol for experiments No. 1 and 2, 1.1 mole for No. 3, 1 mole for Nos. 4-6 and 8-11, and 0.2 mole for No. 7. The solution was added steadily in drops to alcohol in a 0.75-liter flask heated to the required temperature. The solutions were stirred in all experiments. The solution was added over the period indicated in the tables and then the reaction mixture was heated at the given temperature for a further ~1-1.5 hr. The water liberated during the reaction was condensed in a condenser and removed from the reaction zone through a special outlet. The peroxide decomposition products, excess starting alcohol, and 1:1 adduct were distilled from the reaction mixture. The lactone (1:1 adduct) yield was determined after redistillation. The total amount of high-boiling products remaining in the flask after distillation of the 1:1 adduct and after its redistillation is given in Tables 1 and 2.

The molecular weights were determined from the hydrolysis numbers, and for this purpose a sample of lactone was boiled for ~2 hr with 0.6 N KOH solution and then titrated with 0.1 N HCl solution. To determine the purity of one of the reaction products, namely, γ -octylbutyrolactone, we boiled the latter with 10% KOH to form the sodium salt of γ -hydroxylauric acid, which was reconverted to the lactone by treatment with hydrochloric acid and distillation. The properties of the lactone were unchanged.

By a method described previously [7], γ -phenylbutyrolactone (experiment 6) was converted into γ -phenyl- γ -hydroxybutyric acid, which had m. p. 75-76° after recrystallization from warm water; literature data: m. p. 75° [6] and 111-112° [7].

After recrystallization from a benzene-heptane solution, the amide of γ -phenyl- γ -hydroxybutyric acid had m. p. 85-86°; literature data: m. p. 85.5-86.5° [7] and 86° [9].

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*As in original - Publisher.

DIAGRAM OF FERRIC CHLORIDE EXTRACTION WITH DIETHYL ETHER

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January, 1961

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The extraction of ferric chloride from hydrochloric acid solutions with diethyl ether has been the subject of many investigations. However, available data are inadequate for a more or less complete description of the extraction system $\text{FeCl}_3 - \text{HCl} - \text{H}_2\text{O} - (\text{C}_2\text{H}_5)_2\text{O}$. The present investigation was undertaken for constructing the extraction diagram describing this quaternary system. The method of constructing the diagram was examined

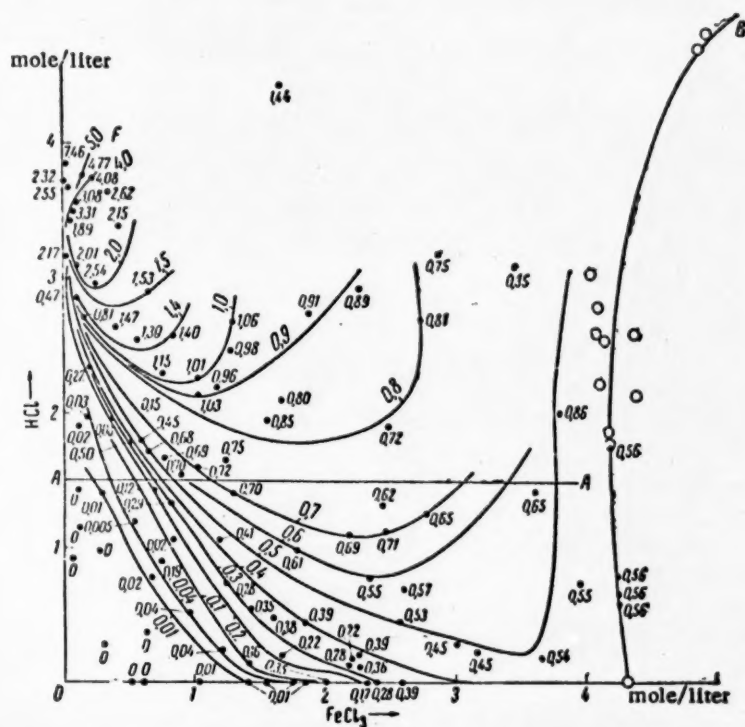


Fig. 1. Diagram of ferric chloride extraction in the system $\text{FeCl}_3 - \text{HCl} - \text{H}_2\text{O} - (\text{C}_2\text{H}_5)_2\text{O}$.

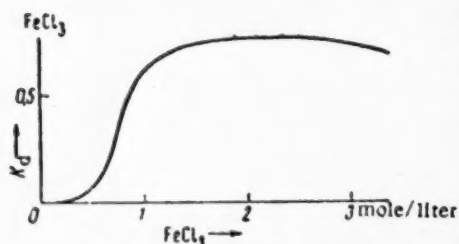


Fig. 2. Relation of K_d of ferric chloride to the ferric chloride concentration in its extraction from solutions in 1.5 M HCl (cross section A-A, Fig. 1).

and then the rate of increase of K_d fell again. The typical curve given in Fig. 2 shows the relation of K_d to the equilibrium FeCl_3 concentration at a constant HCl concentration of 1.5 M (constant concentration cross section A-A in Fig. 1). The threshold FeCl_3 concentration at the given acidity was close to 0.6 M. The FeCl_3 concentration required to reach the extraction threshold decreased with an increase in the acid concentration. The extraction threshold disappeared completely at high acid concentrations, beginning with 2.5 M. The threshold effect was also observed in the absence of HCl, and the maximum threshold concentration of FeCl_3 , which was close to 2.3 M, corresponded to this case.

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RADIOCHROMATOGRAPHY OF ORGANOMERCURY COMPOUNDS

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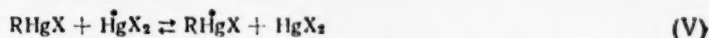
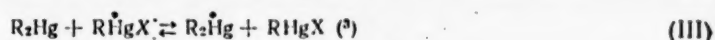
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 2, pp. 366-368,

January, 1961

Original article submitted September 16, 1960

In the last 5-6 years there has been a considerable increase in the amount of work on organometallic compounds, which are very convenient subjects for studying the mechanism of electrophilic and homolytic substitution at a carbon atom.

During a systematic study of reactions (I-VI), which involve isotopic exchange of organomercury compounds,



we repeatedly encountered experimental difficulties in the separation of the reactants, which often had very similar solubilities. It was necessary to develop a method of separating organomercury compounds from each other and from inorganic mercury salts that was suitable for kinetic measurements. Such a method, which is based on radiochromatography, is described in the present paper. As models we chose mixtures of esters of various α -bromomercuriarylacetic esters $XC_6H_4CH(HgBr)COOR$ and mercuric bromide.

It was found that organomercury salts are readily separated from mercuric bromide by chromatography on paper* impregnated with a 10% acetone solution of ethylene glycol (paper treated several hours before use). Various solvents could be used as the mobile phase. The best separation was attained with octane-benzene mixture (3:2 by volume). In this case the mercuric bromide remained at the origin, while the organomercury compound moved directly behind the solvent front. A front movement of approximately 4-5 cm was sufficient for a good separation and this required less than 5 min. If the substances were deposited on the chromatogram as pyridine solutions then the mercuric bromide spot remained only slightly behind the spot of the organomercury compound and a chromatogram length of 8-9 cm was required in this case.

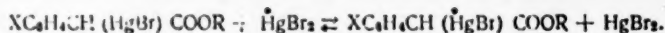
* We should note that there are isolated examples of chromatography of organometallic compounds given in the literature. In particular, there is only one communication [5] on organomercury compounds and this deals with chromatography of substances of the type $RHgCl$, where $R = CH_3, C_2H_5$. No quantitative chromatographic measurements have been described. [Third R in series above given as in Russian - Publisher.]

The zones were developed with a dilute solution of dithizone in chloroform or carbon tetrachloride, which gave a lilac-pink color with organomercury salts and a pink-yellow color with mercuric bromide [6].

We separated mixtures of the organomercury salts $\text{XC}_6\text{H}_4\text{CH}(\text{HgBr})\text{COOR}$ and $\text{YC}_6\text{H}_4\text{CH}(\text{HgBr})\text{COOR}$ for two examples: $\text{X} = \text{H}$ and $\text{Y} = \text{p-Br}$ and also $\text{X} = \text{p-Br}$ and $\text{Y} = \text{o-CH}_3$. The separation was carried out in a reverse phase, for which we used a 10% solution of olive oil in ligroin. The mobile phase was aqueous (60-80%) ethanol or methanol. The relation of R_f to alcohol concentration was as follows:

X	65% $\text{C}_2\text{H}_5\text{OH}$	70% $\text{C}_2\text{H}_5\text{OH}$	80% CH_3OH
H	0,19	0,20	—
p-Br	0,07	0,09	0,18
o-CH ₃	—	—	0,30

We used radiochromatography for studying the kinetics of isotopic exchange of ethyl α -bromomercuriarylacetates with mercuric bromide, labeled with Hg^{203} , in pyridine and 70% aqueous dioxane [7].



The procedure below was used for the work.

Samples of organomercury salt and mercuric bromide were dissolved separately in pyridine or aqueous dioxane, kept at the experimental temperature, and mixed. The total volume of the reaction mixture was 4 ml and the amounts of the substances did not exceed 30-70 mg. A sample was removed with a glass capillary (each capillary was used to remove only one sample) and deposited on paper.* In the case of kinetic measurements, the solution was deposited not as a spot, but a band on a narrow strip of paper (1 cm wide). This gave constant geometry of the spots and thus considerably decreased the error in radiochemical measurements on end-window counters. The degree of exchange was calculated from the ratio of the activity of the zones corresponding to the organomercury compound and mercuric bromide on each paper,

$$F = \frac{A_{\text{Hg-OC}}}{A_{\text{Hg-OC}} + A_{\text{HgBr}_2}} \cdot \frac{C_{\text{Hg-OC}} + C_{\text{HgBr}_2}}{C_{\text{Hg-OC}}}$$

and this eliminated the need to take constant sample volumes. (The subscript Hg - OC denotes the organomercury compound, A represents the activity, and C the concentration.)

Special experiments showed that secondary exchange did not occur on paper under our conditions.

The results obtained by chromatography agreed with results obtained by the normal method, i.e., preparative isolation of one of the substances and subsequent measurement of its activity, and this is shown by the following data:

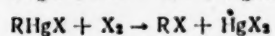
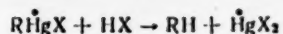
Time (min)	35	60	100	205	405
Degree of exchange (%)					
preparative	5,0	8,2	13,0	24,0	53,5
chromatography	5,0	8,7	12,9	22,5	55,5

It should be noted that at high degrees of exchange (above 70%), the agreement of results in parallel chromatographic tests decreased considerably in many cases and the discrepancy increased.

A comparison of these methods leads to the conclusion that radiochromatography has considerable advantages, namely simplicity, ease, and economy in time (it is possible to work approximately 4 times faster) and materials (a tenth of the normal amounts are needed and this is particularly important with difficultly accessible compounds); naturally, lower activities are used. An important merit is the complete independence of the method of the nature of the solvent, which often hampers quantitative preparative separation.

This method may find application in the study of the kinetics of isotopic exchanges of types II, III, V, and VI and perhaps also the kinetics of reactions of organomercury salts with acids and halides with radioactive RHgX used.

* Leningrad paper, type B.



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INFRARED SPECTRAL STUDY OF THE STRUCTURE OF ETHER-ORGANOLITHIUM COMPOUND COMPLEXES

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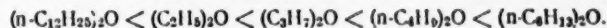
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 2, pp. 369-372,
January, 1961

Original article submitted September 14, 1960

Our previous investigations showed that organolithium compounds are covalent and form complexes [1]. On the basis of our own and literature data, we concluded that the nature of these compounds is evidently close to that of boron, beryllium, and aluminum compounds and results from generalization of the valence electrons of the C-Me bonds with the formation of multicentered orbitals involving free p-orbitals of the metal atom. If lithium actually may be included in one series with Be, B, and Al with respect to complex formation, then one might expect that other types of complex which have been investigated for Be, B, and Al compounds would be formed by organolithium compounds. Thus, Be, B, and Al compounds are known to form complexes of the acceptor-donor type by direct filling of the free p-orbital of the metal atom by an unshared electron pair belonging to the donor molecule [2, 3, 4]. As the investigations showed, the stability of such complexes depends on the donor strength of the parent and falls in the series:



Organolithium compounds also form complexes with ethers and amines [5, 6, 8], but there have been no detailed investigations of these complexes. It is only known that the stability of ether solutions of organolithium compounds depends to a great extent on the structure of both the ether and the organolithium compound and increases in the series [7]:



Moreover, the reaction of organometallic (in particular, organolithium) compounds with ethers, amines, etc., is not only of theoretical interest, as small additions of such donor molecules lead to a sharp decrease in the reactivity of organometallic compounds, and this is evidently connected with a change in the nature and strength of the complexes. The elucidation of this problem could be of some use in controlling the course and rate of the reaction.

The purpose of the present work was to use infrared absorption spectra to determine the effect of esters on the structure and nature of complexes of organolithium compounds. The spectra were plotted on a double-beam N-800 infrared spectrometer with an NaCl prism in the region of 2000 to 650 cm^{-1} in a 100- μ cell.

All the substances studied were either dissolved in ethers or obtained directly in them, with the presence of a large amount of LiBr in the latter case producing no appreciable changes in the spectral region studied. Some organolithium compounds were also studied in benzene solutions with the gradual addition of ethers. The spectra obtained were compared with data from our previous work [1], which made it possible to relate absorption bands to vibrations of C-Li...O groups.

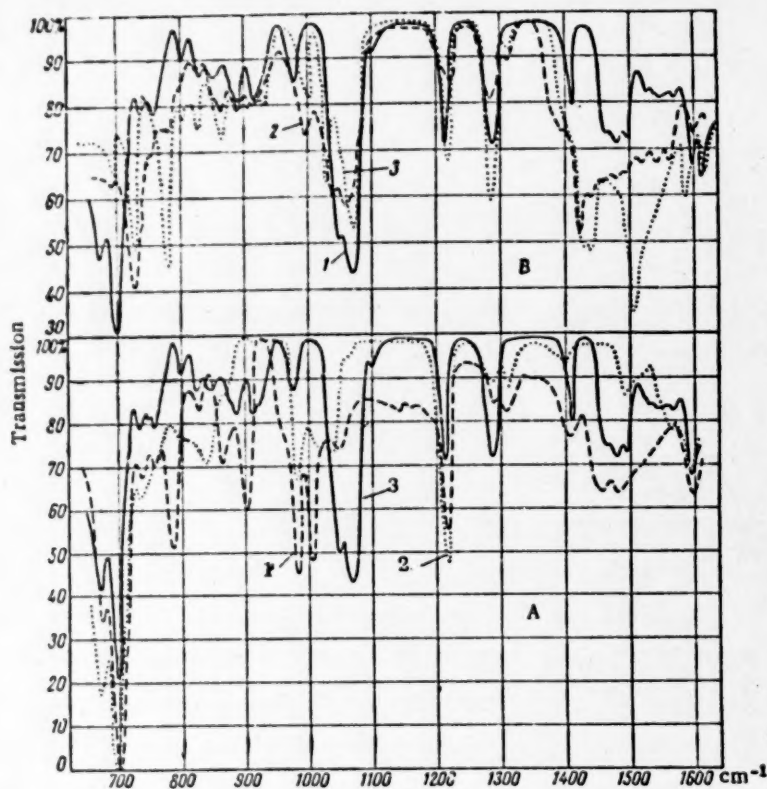


Fig. 1. A) Infrared spectra of solutions of phenyllithium in the following ethers: 1) diethyl ether (0.75 N); 2) dipropyl ether (1.16 N); 3) dibutyl ether (0.67 N). B) Infrared spectra of solutions of aromatic organolithium compounds in dibutyl ether: 1) phenyllithium (0.67 N); 2) o-tolylithium (0.91 N); 3) p-tolylithium (0.8 N). NaCl prism; $d = 100 \mu$.

C-Li Vibration Frequencies in cm^{-1}

Exp. No.	Compound	$(\text{C}_2\text{H}_5)_2\text{O}$	$(n\text{-C}_3\text{H}_7)_2\text{O}$	$(\text{iso-C}_3\text{H}_7)_2\text{O}$	$(n\text{-C}_4\text{H}_9)_2\text{O}$	$(\text{iso-C}_4\text{H}_9)_2\text{O}$
1	Methylithium	966(4);	1668(7);	860(2);	975(2)	—
2	Ethyllithium	895(6);	994(2);	885(4);	—	966(3); 1645(5)
3	n-Butyllithium	966(6);	995(7);	1044(2);	—	893(6);
4	Phenyllithium	966(6);	978(6);	1042(7);	—	1063(5)
5	o-Tolylithium	966(4);	967(2);	1069(6);	970(6)	1054(4); 1073(4)
6	m-Tolylithium	968(3);	998(4)	905(4); 920(1);	1067(5)	1065(4)
7	p-Tolylithium	966(2);	995(6)	1040(4);	—	1063(4)
8	p-Cl-phenyllithium	—	—	973(4)	—	—
9	p-Br-phenyllithium	—	—	—	968(7)	1063(4)
10	Mesityllithium	—	—	—	963(7)	1067(6)
11	Fluorenyllithium	—	—	—	—	1080(5)
		966(3);	975(4);	998(1)	973(5)	1072(3)

An examination of the data obtained (table) shows that the spectra of freshly prepared solutions of almost all the organolithium compounds studied in the same ether showed a similar picture (Fig. 1B). Replacement of one ether by another had a strong effect on the position of the bands that we assigned to C-Li...O groups (Fig. 1A).

Analysis of the spectra shows that with elaboration of the hydrocarbon radicals in the ethers there was displacement of the bands of the C-Li...O groups toward short wavelengths. Thus, while in the spectra of all the

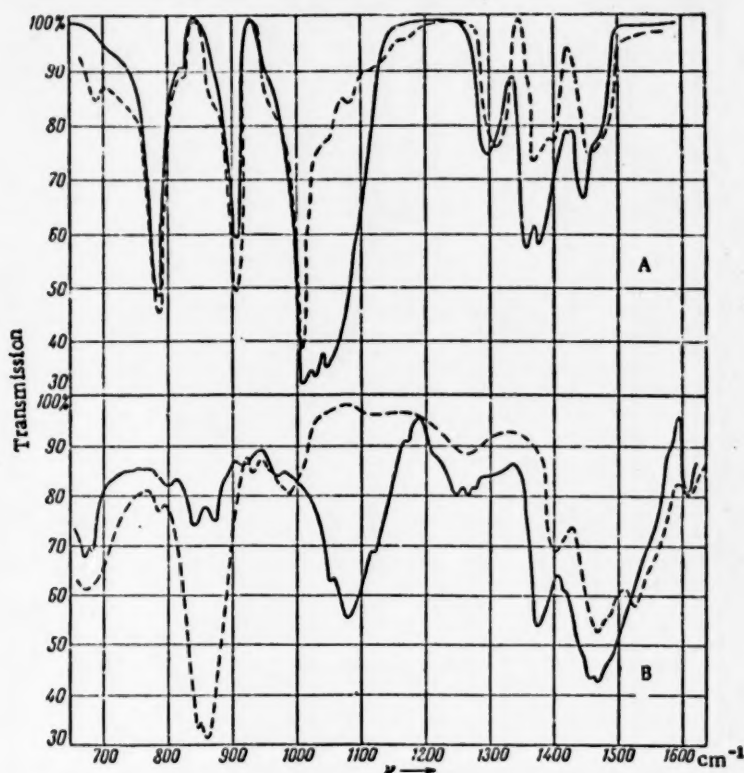
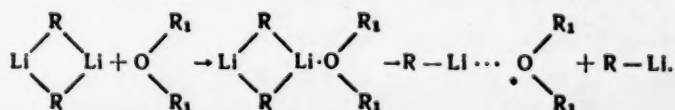


Fig. 2. A) Infrared spectra of solutions of methyllithium in diethyl ether (0.78 N): 1) fresh solution; 2) solution kept under argon for 7 days. B) Infrared spectra of solutions of mesyllithium in dibutyl ether: 1) dissolved at 20°; 2) dissolved at 120°. NaCl prism; $d = 100 \mu$.

organolithium compounds investigated in diethyl ether there were the most displaced bands at about 900 cm^{-1} , in dipropyl and diisopropyl ethers these were at 970 cm^{-1} , and in dibutyl and diisooamyl ethers there was only one intense band at about $1050\text{--}1090 \text{ cm}^{-1}$, which we ascribed to a free or weakly bound C-Li group. This is evidently due to steric hindrance to a sufficiently close approach of the molecules for the formation of a complex. Due to the equal donor strengths of aliphatic ethers, in this case the final result for all cases should be complexes of similar strengths (analogous to etherates of organoaluminum compounds [4]), but their formation proceeds the more slowly, the more complex the structure of the ethers and the molecules of the organolithium compound.

Thus, while the most active organolithium compound, ethyllithium, forms a complex absorbing at about 900 cm^{-1} almost immediately in all ethers, this process takes time with more complex and less active molecules. In actual fact, when a solution of *o*-tolyllithium in dibutyl ether was kept under argon for several days there was a fall in the intensities of the bands of free and weakly bound C-Li groups ($1040\text{--}1060 \text{ cm}^{-1}$) and an increase in the intensity of the band at about 900 cm^{-1} . This was also observed in the case of methyllithium and *n*-butyllithium in diethyl ether (Fig. 2A). The formation of a strong complex could be accelerated by raising the solution temperature, as is shown by Fig. 2B.

Thus, in the solution of organolithium compounds in ethers apparently there is first deformation and decomposition of the primary complexes due to donor-acceptor and dipole interaction with the ether and then there is the gradual (depending on the structure of the radicals of both components) formation of new complexes between molecules of ether and organolithium compound of the donor-acceptor type.



With an increase in the strength of the new complexes, there is an increase in the polarity of the C-Li bond, and this must show as a change in the reactivity of the organolithium compound and the stability of the latter in solution. This is probably the reason for the high reactivity of ethyllithium in many reactions in ether and its low stability in this medium.

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HYDROGENATION OF FURAN DERIVATIVES CONTAINING A CARBONYL GROUP

CONVERSION OF 2-ALKYL-5-ACYLFURANS TO 2,6-DIALKYL-TETRAHYDOPYRANS

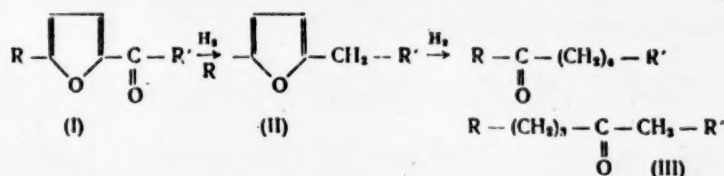
I. F. Bel'skii, Corr. Member AN SSSR N. I. Shulkin, and
G. K. Vasilievskaya

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 3, pp. 591-594,
January, 1961

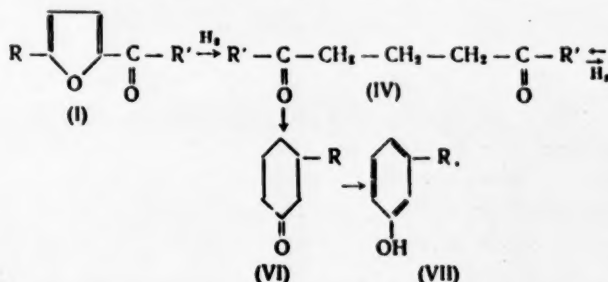
Original article submitted October 21, 1960

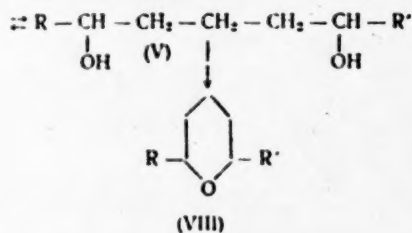
During catalytic hydrogenation in the vapor phase, 2-alkyl-5-acylfurans (I) can react in two different ways:

1. The reaction may start with the reduction of the carbonyl group to CH_2 with the formation of 2,5-di-alkylfurans (II). The latter may then undergo hydrogenolysis to the aliphatic ketones (III). Such a reaction pathway is observed, for instance, with skeletal Cu-Al catalyst [1], Ni-ZnO, or Ni-CdO [2]:



2. Hydrogenolysis of the furan ring may precede the reduction of the carbonyl group. The ability to direct the reaction in this way is possessed by platinum catalysts, such as platinum on carbon and platinum on asbestos. We found that upon hydrogenation on a platinum catalyst, the furan ring of 2-alkyl-5-acylfurans is ruptured solely at the C-O bond located beside the carbonyl group [3]. The 1,5-diketones (IV) thus formed are cyclized, under the conditions of vapor-phase hydrogenation, to the mono- and disubstituted homologs of cyclohexanone (VI) or phenol (VII). On platinized charcoal, at 300°, the alkylphenols are obtained in 50-60% yields [4].



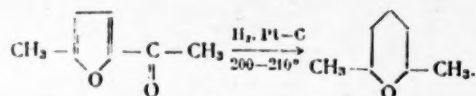


We have shown that if the hydrogenation of 2-alkyl-5-acylfurans is carried out at 200-300°, then the reaction products practically do not contain any phenols; instead, the catalyzate contains cyclohexanone and cyclohexanol homologs. In the present work, the formation of 2,6-dialkyltetrahydropyrans during the hydrogenation of 2-alkyl-5-acylfurans on a platinum catalyst is reported for the first time.

The 1,5-diketones formed as primary hydrogenolysis products of 2-alkyl-5-acylfurans may either cyclize to six-membered carbocyclic compounds [4] or, depending on the temperature conditions, become hydrogenated to the corresponding 1,5-alkane-diols (V), which by intramolecular loss of water give tetrahydropyrans (VIII). The equilibrium diketone \rightleftharpoons diol is shifted in the direction of the diol with lowering of temperature; it follows that the formation of tetrahydropyrans will be favored by low temperature. Actually, as our experiments show, the highest yields of tetrahydropyrans are obtained at 200-220°, while at 300-350° tetrahydropyrans are practically absent in the reaction products.

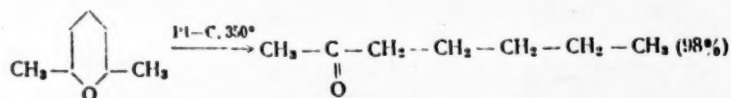
Another factor favorable to a more thorough transformation of 1,5-diketones to 1,5-diols is the increase of hydrogen pressure during hydrogenation. However, our experiments on the hydrogenation of 2-methyl-5-acetylfuran on Pt-C in a flowing system under 50 atm pressure of hydrogen showed that under such conditions the primary reaction is not the hydrogenolysis of the furan ring, but the reduction of the carbonyl group, followed by the hydrogenation and hydrogenolysis of the furan ring [5].

Conversion of 2-methyl-5-acetylfuran to 2,6-dimethyltetrahydropyran. Hydrogenation of 2-methyl-5-acetylfuran [b. p. 68-69° (VII), n_D^{20} 1.5090, d_4^{20} 1.0655] on Pt-C at 200-210° and normal pressure with a space velocity of 0.1 hr⁻¹ gave 2,6-dimethyltetrahydropyran with a 25-35% yield:



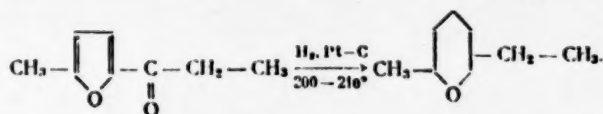
2,6-Dimethyltetrahydropyran appeared in the fraction boiling at 111-113°. The refractive index of this fraction varied from n_D^{20} 1.4195 in an experiment carried out at 200° to n_D^{20} 1.4220 in an experiment at 220°. This showed that this fraction contained some products other than 2,6-dimethyltetrahydropyran. Spectral analysis of this fraction boiling between 111 and 113° revealed the presence of toluene. As reported by us earlier [4], the latter is formed by reduction of m-cresol, which in turn is produced by the cyclization of 1,5-heptanedione (the primary hydrogenolysis product of 2-methyl-5-acetylfuran). In order to prepare 2,6-dimethyltetrahydropyran in a purer state, the fraction with b. p. 111-113° was submitted to hydrogenation on Pd-C at 180° in a flowing system, in order to convert the toluene to methylcyclohexane. After fractional distillation of the catalyzate with an efficient column over Na, the 2,6-dimethyltetrahydropyran had b. p. 112-113° (750 mm), d_4^{20} 0.8384, n_D^{20} 1.4180.

2,6-Dimethyltetrahydropyran was then isomerized to 2-heptanone on Pt-C, in the vapor phase at 350°:



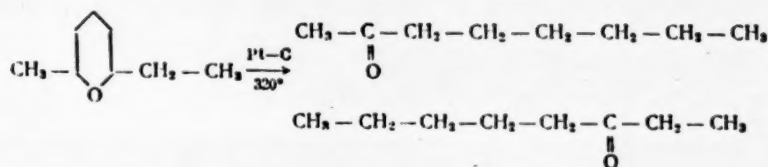
The 2-heptanone thus obtained had b. p. 148-150° (745 mm), n_D^{20} 1.4096, d_4^{20} 0.8160, and it gave a semi-carbazone derivative, m. p. 121°.

Conversion of 2-methyl-5-propionylfuran to 2-methyl-6-ethyltetrahydropyran. 2-Methyl-5-propionylfuran [b. p. 68-70° (3 mm), n_D^{20} 1.5032, d_4^{20} 1.0394] was hydrogenated by the flow method on Pt-C at 200-210°.

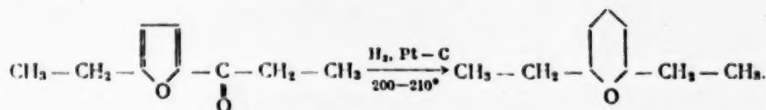


2-Methyl-6-ethyltetrahydropyran, obtained with a yield of about 20%, was found in the fraction boiling at 133-136°; d_4^{20} 0.8485, n_D^{20} 1.4300. Spectral analysis of this fraction revealed the presence of traces of ethylbenzene and o-xylene. These hydrocarbons were obviously formed in the same way as toluene during the hydrogenation of 2-methyl-5-acetylfuran.

Isomerization of 2-methyl-6-ethyltetrahydropyran in the vapor state on Pt-C at 320° gave a mixture of 2-octanone and 3-octanone:

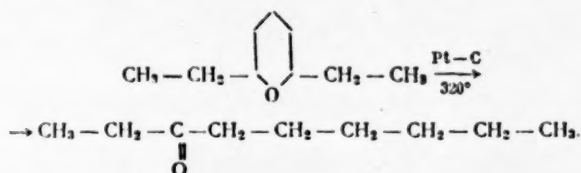


Conversion of 2-ethyl-5-propionylfuran to 2,6-diethyltetrahydropyran. 2,6-Diethyltetrahydropyran was obtained with a 20% yield by the hydrogenation of 2-ethyl-5-propionylfuran [b. p. 107-108° (16 mm); n_D^{20} 1.5000, d_4^{20} 1.0152] in a flowing system on Pt-C at 200-210°.



2,6-Diethyltetrahydropyran belonged to the fraction boiling at 155-158°; d_4^{20} 0.8489, n_D^{20} 1.4353.

As a result of isomerization of this fraction in the vapor phase on Pt-C at 320°, 3-nonanone was obtained with a 90% yield, b. p. 190-191° (755 mm); d_4^{20} 0.8230, n_D^{20} 1.4210.



It is possible that the tetrahydropyrans obtained in these experiments were contaminated with insignificant amounts of cyclohexane derivatives corresponding to the aromatic hydrocarbons formed as by-products during the hydrogenolysis of 2-alkyl-5-acylfurans on Pt-C (see above). This is all the more possible since the temperature under which tetrahydropyrans are formed is also favorable for the conversion of the benzene ring into a cyclohexane ring.

In conclusion, it must be emphasized that a further study of the hydrogenation of ketones of the furan series can lead to a new general method for the synthesis of the difficultly accessible homologs of tetrahydropyran.

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STEREODIRECTED SYNTHESIS WITH DIACETYLENE;
ISOMERIZATION OF 1,4-BIS-(ARYLTHTIO)-1,3-BUTADIENES
AND THEIR SULFONES

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and G. I. Plotnikova

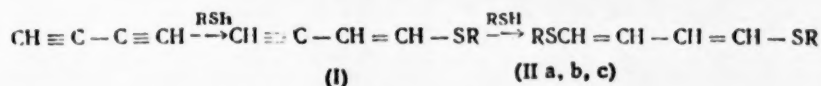
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In our previous works [1-3] we have studied the reaction of diacetylene with alcohols and mercaptans and shown the stepwise character of this reaction. With mercaptans, the first products formed are ethynylvinyl thioethers, which are followed by 1,4-bis-(alkyl,aryl)-thio-1,3-butadienes. At the same time, it was found that the first step of the reaction occurs according to an ionic mechanism, while the second step of the reaction proceeds mostly according to the free-radical mechanism [2-4].



During spectroscopic studies of the diacetylene derivatives isolated from these reactions, we [5] and then other authors [6] observed the formation of mixtures of stereoisomers of 1,4-bis(alkyl,aryl)-thio-1,3-butadienes; this observation prompted us to investigate the syntheses starting with diacetylene from the point of view of their stereorientation, especially as this question has not been studied at all until now. Studies of the conditions for stereodirected syntheses from acetylene and vinylacetylene are known [7, 8]; on the other hand, Truce [9] has described the ionic addition of mercaptans to monoacetylenes. These authors concluded that this reaction obeys the rule of transnucleophilic addition. The stereochemistry of the addition reactions of substituted acetylenes has been studied by Nazarov and Bergel'son [10]. The latter authors found that under ionic conditions this reaction proceeds with the formation of cis-olefinic derivatives, whereas under the free-radical conditions it is not stereospecific and depends on the substituents. Inhoffen [1] has investigated the stereochemistry of the synthesis of 1,4-bis-(acetoxy)-1,3-butadienes; the structure of the three isomers which were isolated was proved by spectroscopic means and diene synthesis. Recently, one of us, in collaboration with Prilezhaeva and Tsimbali [12], studied the stereochemistry of the addition reaction of butyl mercaptan to ethynylvinylthiobutyl ether; it was found that under ionic conditions this reaction proceeds in a way analogous to that of substituted monoacetylenes, i.e., following the rule of trans-addition [9]. The authors characterized the isomers of 1,4-bis-(butylthio)-1,3-butadienes by their sulfone derivatives, which they isolated from the oxidized mixture of the former compounds. In a study by one of us with Chekulaeva and Kondrat'eva [13] we also showed the applicability of this rule to the synthesis of N-containing diacetylene derivatives under ionic conditions.

The aim of our work to investigate the conditions of the stereorientation in the synthesis of 1,4-bis-(arylthio)-1,3-butadienes from diacetylene and aryl mercaptans, to isolate their stereoisomers, and also to study some of their properties and reactions. For this purpose we chose thiophenol, which forms with diacetylene crystalline stereoisomeric 1,4-bis-(phenylthio)-1,3-butadienes. We carried out the synthesis of these compounds

TABLE 1

No.	Catalyst, solvent	Temp. of expt., °C	Duration, hr	Yield, %	M. p., °C; product
1*	KOH, hydroquinone, dioxane, alcohol	30-35	12	40.0	81-82° IIa
2**	Air oxygen, heptane	70	12	43.7	40-41° IIb and IIc
2a	" " "	35	12	8	40-41°; IIb and IIc
3***	KOH, air oxygen, dioxane, alcohol	35-70	9	19.7 26.2± ±23.1	81-82°; IIa 81-82°; IIa 40-41°; IIb and IIc
4*	Air oxygen, heptane (from ethynylvinylthiophenyl ether)	70	12	80.0 on I	40-41°; IIb and IIc

* The crystals of IIa, which separated out where the flask was cooled to room temperature, were filtered off, washed with water, and recrystallized from alcohol to constant m. p. same procedure in all cases).

** The mixture of IIb and IIc was obtained by recrystallization from alcohol of the residue left after the removal of heptane and thiophenol by vacuum distillation.

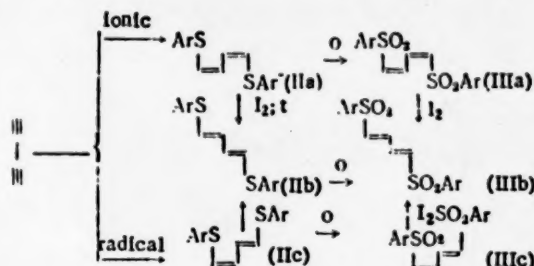
*** The reaction was carried out at 35° for 6 hr; the mixture was then left to stand overnight at room temperature and finally heated at 70° for 3 hr. IIa was isolated as in Expt. 1. Upon addition of water to the dioxane solution, an uncrystallizable oil separated out; by vacuum distillation, this oil gave a mixture of IIb and IIc.

TABLE 2

Stereoisomer obtained Ar = C ₆ H ₅	M.p., °C	Configuration ascribed	Found, %			Calculated, %		
			C	H	S	C	H	S
$\begin{array}{c} \text{ArS} \\ \\ \text{I}=\text{I} \\ \\ \text{SAr} \end{array} \quad \text{IIa}$	81-82	cis-cis	71.14 71.23	5.20 5.42	23.64 23.89	71.06	5.21	23.71
$\begin{array}{c} \text{ArS} \quad \text{SAr} \\ \quad \quad \\ \text{I}=\text{I} \quad \text{I}=\text{I} \\ \quad \quad \\ \text{IIb} \quad \text{IIc} \end{array}$	40-41	Mixture of trans-trans and cis-trans	71.11 70.88	5.42 5.37	23.70 23.68	71.06	5.21	23.61
$\begin{array}{c} \text{ArSO}_2 \\ \\ \text{I}=\text{I} \\ \\ \text{SO}_2\text{Ar} \end{array} \quad \text{IIIa}$	157.3- 157.8	cis-cis	57.24 57.38	4.18 4.24	19.10 19.15	57.16	4.21	19.17
$\begin{array}{c} \text{ArSO}_2 \\ \\ \text{I}=\text{I} \\ \\ \text{SO}_2\text{Ar} \end{array} \quad \text{IIIb}$	188- 189	trans-trans	57.15 57.00	4.36 4.45	19.13 18.99	57.16	4.21	19.17
$\begin{array}{c} \text{ArSO}_2 \\ \\ \text{I}=\text{I} \\ \\ \text{SO}_2\text{Ar} \end{array} \quad \text{IIIc}$	112.5- 113	cis-trans	57.31 57.45	4.21 4.24	19.18 19.07	57.16	4.21	19.17

under the conditions of both ionic and radical addition, as well as under the simultaneous operation of both these factors (Table 1). Two crystalline products were obtained, which were oxidized, isomerized, and submitted to optical examination. One of these products appeared to be the pure cis-cis isomer of 1,4-bis-(phenylthio)-1,3-

butadiene (IIa), and the other product was a mixture containing 80% of IIb and 20% of IIc. This mixture was resolved after oxidation under conditions excluding the possibility of isomerization. As a result, we obtained the three possible isomers of 1,4-bis-(phenylsulfone)-1,3-butadiene (IIIa, IIb, IIc), the stereochemical reactions of which were investigated. The isomers obtained (Table 2) were assigned the configurations which conform to their physical properties and isomerization reactions, according to the following scheme, where Ar = C₆H₅.



The cis-cis structure of IIa is proved by its quantitative isomerization to a mixture of IIb and IIc, effected either by heating or under the influence of iodine and light—such a behavior is characteristic for 1,4-bis-substituted 1,3-butadienes [7, 11]; this structure is further confirmed by the preparation of the sulfone IIIa from IIa, with a quantitative yield. The product melting at 40–41° is a mixture of IIb and IIc, as by oxidation it gives a mixture of sulfones easily resolvable to IIb and IIc; this is the case with other butadiene sulfones [11]. The relation between the melting points of the isolated isomers IIa, IIb, and IIc, and IIIa, IIb, and IIc is characteristic for the already investigated [7, 13] substituted 1,3-butadienes, i.e., the substance with the lowest melting point is the cis-trans isomer, and the one with the highest melting point is the trans-trans isomer.

Mixed samples do not display a melting point depression, but melt over broad temperature ranges. The smoothly occurring isomerization with iodine [7, 11], by which IIIa and IIc are converted into IIb, also confirms the structures attributed to these substances.

The ultraviolet spectra of all the isolated isomers show an absorption band in the 240 mμ range; this is a confirmation of their butadiene structure. The infrared spectrum of IIIa has absorption bands at 702 and 760 cm⁻¹, which are missing in the spectrum of IIb, while IIb has a very intense band at 992 cm⁻¹, which is missing in the spectrum of IIIa. The infrared spectra of IIc show absorption bands at 697, 765, and 992 cm⁻¹, which are common to IIIa and IIb. All the absorption bands found in these spectra are characteristic for the geometrical isomers of butadiene derivatives which were studied previously [11–13].

Therefore, the study of syntheses with diacetylene and thiophenol under different conditions shows the possibility of carrying out these reactions with a given stereorientation. Thus, under ionic conditions (expt. 1), we effected the stereospecific synthesis of cis-cis-1,4-bis-(phenylthio)-1,3-butadiene (IIa), whereas under the conditions of free radical addition of thiophenol to diacetylene, and under mixed conditions, we obtained a mixture of all the three isomers, the relative amounts of which depended on the reaction temperature (expts. 2 and 2a). The free-radical addition of thiophenol to ethynylvinylthiophenyl ether (I), which smoothly forms a single bis-mercuroacetylenide (Ia), leads to the formation of a mixture of IIb and IIc (expt. 4).

The results obtained show that the reaction of diacetylene with thiols under ionic conditions occurs with the addition of two molecules of the thiol to the two acetylenic linkages, similarly to the addition of thiols to mono- [9, 10] and disubstituted [10] acetylenes, i.e., according to the rule of the "transnucleophilic addition"; thus, the reaction occurs according to the same rules as the addition reaction of butyl mercaptan to ethynylvinylthiobutyl ether [12]. Under the conditions of a free-radical reaction of diacetylene with thiophenol, the reaction we are concerned with occurs in a nonstereospecific manner, i.e., it proceeds with the formation of a mixture of isomers.

Diacetylene and ethynylvinylthiophenyl ether (I) were synthesized according to our already reported method [1]. Bismercuroacetylenide, Hg(C≡C-CH=CH-SC₆H₅)₂ (Ia), was prepared as reported [2, 12] with a 75% yield; m. p. of Ia: 165.5–168° (from toluene).

Found %: C 46.78; H 2.90; S 12.24. C₂₀H₁₄S₂Hg. Calculated %: C 46.28; H 2.72; S 12.33.

Synthesis of the stereoisomeric 1,4-bis-(phenylthio)-1,3-butadienes. IIa, IIb, and IIc were synthesized from diacetylene (4 g) and thiophenol (18 g) (molecular ratio 1:2) in a flask fitted with a stirrer and a thermometer. Data concerning the most typical experiments are gathered in Table 1, and the characterization of the isolated isomers is given in Table 2. In expt. 4, the starting materials were ethynylvinylthiophenyl ether (3 g) and thiophenol (4.1 g). The product melting at 81-82° (IIa) was obtained as white needle crystals, stable when kept at room temperature and remaining unchanged upon melting. The product with m. p. 40-41° (mixture of IIb and IIc) occurred as colorless shining platelets, distilling at 200-201° (2.5 mm); upon storage this product darkened rapidly and was transformed into an oil from which crystals of diphenyldisulfide, m. p. 58.5-59°, separated out.

Preparation of cis-cis-1,4-bis-(phenylsulfone)-1,3-butadiene (IIIa). Half a gram (0.0018 mole) of IIa in 7 ml of dry ether was treated, while stirring and cooling to -5° to +3°, with 0.36 g (0.006 mole) of peracetic acid. The mixture was stirred for a further 12 hr; the precipitated IIIa was filtered off, washed with ether, and recrystallized from alcohol. Yield of IIIa; 0.55 g (91.6% of theoretical); m. p. 157.3-157.8° (Table 2).

Fractionation of the mixture of cis-trans and trans-trans isomers (IIb and IIc). Under the conditions for oxidation described above, 0.5 g of the product with m. p. 40-41° gave a total of 0.5 g (84% of theoretical) of disulfones. The precipitate which separated from the reaction mixture was isolated, washed with water, and recrystallized from alcohol. M. P. of IIIb, 188-189°; yield 0.4 g (corresponding to 80% of the sulfone mixture). From the ethereal solution was obtained 0.09 g (18%) of IIIc, m. p. 112.5-113° (from alcohol).

Isomerization of cis-cis-1,4-bis-(phenylthio)-1,3-butadiene (IIa). One and a half grams of IIa was heated in a flask fitted with a reflux condenser for 30 min at 200°. After cooling, the product was recrystallized from alcohol. The mixture of IIb and IIc thus obtained melted at 40-41°; yield 1.4 g (93%).

Found %: C 70.61, 70.55; H 5.27, 5.19; S 23.49, 23.57. $C_{16}H_{14}S_2$. Calculated %: C 71.06; H 5.21; S 23.71.

IIa (0.10 g) in 2 ml of dioxane containing a small crystal of iodine was irradiated with a daylight lamp for 1.5 hr at 25-30°. After removal of the dioxane, the residue was washed with water and crystallized from alcohol, giving 0.095 g (95%) of product with m. p. 40-41°. The yield of this product decreased upon prolonged irradiation, and diphenyldisulfide, m. p. 58-59°, was then isolated from the residue. The isomerization of IIa took place also during its vacuum distillation.

Isomerization of cis-cis-1,4-bis-(phenylsulfone)-1,3-butadiene (IIIa). A solution of IIIa (0.1 g) in dioxane containing iodine was exposed to sunlight for 2 days. Working up the product gave 0.99 g of IIIb, m. p. 188-189° (from alcohol), causing no depression of melting point when mixed with pure IIIb.

Isomerization of cis-trans-1,4-bis-(phenylsulfone)-1,3-butadiene (IIIc). A solution of IIIc (0.05 g) with m. p. 112.5-113° in dioxane containing iodine gave, after illumination with a quartz lamp for 3 hr, 0.05 g of IIIb, m. p. 188-189°, giving no depression of melting point when mixed with analytically pure IIIb.

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KINETICS AND MECHANISM OF THE REACTION OF ALUMINUM ALKYLS WITH TITANIUM HALIDES

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It has been shown recently in a series of studies [1-3] that when aluminum alkyls are reacted with *i*-dicyclopentadienyltitanium dichloride, soluble products, which are capable of catalyzing the polymerization of ethylene, are formed. In our previous article [4] we presented data on the structure of the paramagnetic complexes which are the final products of this reaction. Although ethylene polymerization does proceed in the presence of these complexes their activity is considerably less than that of a reacting system such as, for instance, $(C_5H_5)_2TiCl_2 - Al(C_2H_5)_2Cl$. Thus the most active particles are formed and disappear during the reduction of Ti^{4+} . It was therefore of considerable interest to elucidate in detail the mechanism of the reaction of aluminum alkyls with halides of titanium, determining at the same time the structure of the particles participating in the reduction process. In this study we present results for the reaction of $(C_5H_5)_2TiCl_2$ with $Al(C_2H_5)_3$, $Al(CH_3)_3$ and $Al(C_2H_5)_2Cl$ and we make an attempt to devise a mechanism for the process by combining our own and published data.

I. Reaction of $(C_5H_5)_2TiCl_2$ with $Al(C_2H_5)_3$. In this reaction, which proceeds very rapidly, titanium is reduced with the formation of a blue complex in accordance with the following scheme:



The quantity of ethane formed is equivalent to half the $(C_5H_5)_2TiCl_2$ taken, which corresponds to disproportionation of the ethyl groups. The ethylene obtained is always less than the ethane; formation of butane is not observed. Aluminum alkyls react similarly with $TiCl_4$. The difference lies in the fact that Ti is reduced in this case to lower valence states than $3+$, and therefore at not very high Al:Ti ratios the alkane formed is one half of the Al taken, not of the Ti as in the case of $(C_5H_5)_2TiCl_2$. The reduction of the yield of ethylene in comparison with ethane is usually explained by partial polymerization of ethylene. We found that butane is obtained on decomposing the reaction products from $(C_5H_5)_2TiCl_2$ and $Al(C_2H_5)_3$ with water [about 20% butane with respect to the amount of $(C_5H_5)_2TiCl_2$ taken], which may be interpreted in conventional terms as corresponding to the introduction of only a single ethylene molecule at a Me-C linkage during the reduction process.

II. Reaction of $(C_5H_5)_2TiCl_2$ with $Al(CH_3)_3$. In this case when toluene solutions of the reactants are mixed reduction of titanium proceeds slowly without the formation of a blue complex of type IV. If the reaction is carried out in the presence of ethylene a rapid change of color from red to blue occurs, and at the same time methane is liberated, accompanied by condensation of ethylene. It was found that the blue complex formed could be distilled off. Analysis of the crystals obtained, the visible spectrum and the electron paramagnetic resonance spectrum indicate that the product has a structure similar to IV and a composition $(CH_3)_2AlCl \cdot (C_5H_5)_2TiCl$. It was found that other α -olefins - propylene, butylene-1, amylene-1 - also react in a similar fashion. Unlike ethylene, which condenses to an appreciably greater extent than one mole per mole of titanium,

in the case of the other α -olefins mentioned condensation occurs in approximately equimolecular proportions. On hydrolysis of the products of this reaction when carried out in the presence of propylene a considerable amount of butane was liberated, while on hydrolysis of the products of the reaction carried out in the presence of ethylene, propane and butane are obtained. Thus the reaction also proceeds in this case in accordance with the conventional scheme involving disproportionation of alkyl groups, but introduction of the olefin at a Me-C bond occurs first, accompanied by the formation of an alkyl group capable of disproportionation, while the new olefins formed in the disproportionation step are again introduced at a Me-C bond.

In cyclohexane, ethylene condensation, accompanied by simultaneous reduction of the red complex, proceeds several times more slowly than in toluene.

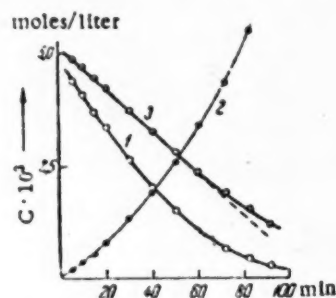


Fig. 1. Kinetics of the reaction of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ with $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ in benzene at 28° . Variation of the concentration C of complex III (1), $\log C_0/C$ (2) and C^{-1} (3) with time (C was determined by optical density at $\lambda = 455 \text{ m}\mu$).

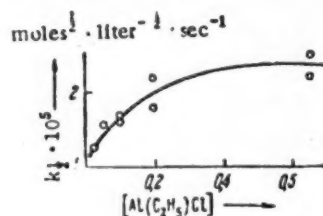
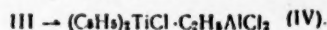
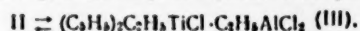


Fig. 2.

Reaction Mechanism

The experimental data quoted refute the idea of a free-radical mechanism for the reduction of titanium halides by aluminum alkyls. If ethane and ethylene were in fact the products of free radical disproportionation, then the formation of butane as the product of their recombination should also be observed. In addition the ethyl radicals would also remove H from the solvent molecules, at any rate from a solvent such as toluene. The quantity of ethane however corresponds exactly to the disproportionation process. In the system $\text{TiCl}_4 - \text{Al}(\text{iso-C}_4\text{H}_9)_3$ it has been shown that the yield of isobutane is not reduced when free-radical acceptors, for example anthracene, are added. The data on the reaction of $\text{Al}(\text{CH}_3)_3$ with $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$, which proceeds slowly in the absence of olefins, and which is hard to explain from the viewpoint of a free radical scheme, also conflict with a free radical mechanism.

III. Reaction of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.^{*} In this case reduction proceeds at a measurable rate. It is convenient to follow the kinetics of the reaction using the variation of the visible spectra as observed in the studies by Breslow and co-workers [1, 3]. In these studies it was shown that the reaction proceeds according to the following scheme:



The slow stage of the reaction is the transition from complex III to complex IV, which is accompanied by change in color from red to blue.

As may be seen from Fig. 1 the reaction is of order 1/2; this holds up to 70-80% conversion. Beyond this the order changes toward unity.

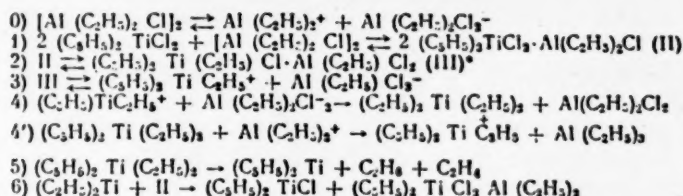
Breslow and Long [3] observed only a reaction of first order. It is possible that this is due to the lower initial concentrations of $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ with which these authors worked. The velocity constant $k_{1/2}$ is weakly dependent on $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ concentration (Fig. 2). If $[\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}]$ is increased 30 times $k_{1/2}$ only increases by a factor of two.

At lower $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ concentrations, where the reaction order with respect to III approaches unity, the reaction rate is completely independent of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ concentration within wide limits.

The velocity constants determined in the range $25-47^\circ$ are equal to: $k_{1/2}$ (in benzene) = $5.25 \cdot 10^6 \exp(-15700/RT) \text{ mole}^{-1/2} \cdot \text{liter}^{-1/2} \cdot \text{sec}^{-1}$; $k_{1/2}$ (in methylcyclohexane) = $1.52 \cdot 10^{11} \exp(-22200/RT) \text{ mole}^{-1/2} \cdot \text{liter}^{-1/2} \cdot \text{sec}^{-1}$.

^{*} Study of the kinetics of this reaction was commenced at Oxford in conjunction with E. W. Randall and L. E. Sutton.

On the other hand many of the data point to the possibility of an ionic mechanism. As we have seen, the reduction of $(C_5H_5)_2TiCl_2$ by diethylaluminum chloride takes place in benzene with a smaller activation energy than in methylcyclohexane. The reaction of $(C_5H_5)_2TiCl_2$ with $Al(CH_3)_3$ in the presence of olefins in toluene solution proceeds appreciably faster than in cyclohexane. This may be due to a reduced ability to ionize in going from benzene and toluene to methylcyclohexane and cyclohexane. It is scarcely possible to explain the reaction order of one half in the case of the reaction of $(C_5H_5)_2TiCl_2$ with $(C_2H_5)_2AlCl$ in any way other than by equilibrium dissociation into the ions of complex III, which is supported by the appreciable increase in electrical conductivity when the complex is formed [5]. We consider that the data quoted regarding the kinetics of this reaction can be interpreted by the following mechanism:



At fairly high $(C_5H_5)_2TiCl_2$ concentrations the reaction rate (v) is determined by stage (5), and thus at a stationary concentration of $(C_5H_5)_2Ti(C_2H_5)_2$

$$v = k_5 [(C_5H_5)_2Ti(C_2H_5)_2] = k_5 \frac{k_4 [(C_5H_5)_2TiC_2H_5^+] [Al(C_2H_5)_2Cl_2^-]}{k_4' [Al(C_2H_5)_2^+] + k_3}$$

At high $Al(C_2H_5)_2Cl$ concentrations, when k_5 may be neglected in comparison with $k_4' [Al(C_2H_5)_2^+]$, and taking into account that $[Al(C_2H_5)_2^+] \approx [Al(C_2H_5)_2Cl_2^-]$, we obtain $v = k_5 (k_4/k_4') [(C_5H_5)_2TiC_2H_5^+]$. Substituting the value of $(C_5H_5)_2TiC_2H_5^+$ concentration determined from equilibrium (3) (taking into account that $[(C_5H_5)_2TiC_2H_5^+] \approx \alpha [Al(C_2H_5)_2Cl_2^-]$) we get: $v = k_5 (k_4/k_4') K^{1/2} \times [III]^{1/2}$, which explains the experimentally determined reaction order and its independence of $Al(C_2H_5)_2Cl$ concentration.

At low $Al(C_2H_5)_2Cl$ concentrations, when $k_5 \gg k_4' [Al(C_2H_5)_2^+]$, $v = k_4 [(C_5H_5)_2TiC_2H_5^+] [Al(C_2H_5)_2Cl_2^-] = k_4 K^{1/2} [III]^{1/2} [Al(C_2H_5)_2Cl]^{1/2}$. Thus, in accordance with experiment the reaction order with respect to $Al(C_2H_5)_2Cl$ should change from $1/2$ to 0.

At low $(C_5H_5)_2TiCl$ concentrations, equilibrium apparently does not have time to establish itself and reaction (3) becomes rate determining. Clearly in this case the reaction should be first order with respect to III, and the reaction rate should be independent of the concentration of $Al(C_2H_5)_2Cl$, if it is present in excess. However if the Al:Ti ratio is reduced to 1:1, when the alkylating $Al(C_2H_5)_2Cl_2^-$ ions are almost absent from the solution, the reaction should be greatly retarded. This is in fact observed, and in addition it is shown in the work of Breslow and Long [3] that the reaction becomes zero order. It is possible that in this case reaction (0) is the rate-determining step, and thus the over-all rate is independent of the concentration of complex III. In any case the zero order kinetics and the marked retardation of the reaction at Al/Ti = 1 rule out the hypothesis of Breslow and Long that decomposition of III to $C_2H_5^+ + (C_5H_5)_2TiCl_2 \cdot Al(C_2H_5)Cl$ occurs, as the reaction rate in that case could not depend on the concentration of the excess $Al(C_2H_5)_2Cl$.

Disproportionation of the alkyl groups takes place, in our view, within the $(C_5H_5)_2Ti(C_2H_5)_2$ molecule. The hypothesis that such a process occurs readily explains the fact that up till now diethyl derivatives of titanium have not been prepared, whereas diphenyl and dimethyl derivatives have been synthesized, as reaction (5) is impossible for these due to the absence of a β -hydrogen atom.

The $Al(C_2H_5)_4^-$ ion in a solution of $Al(C_2H_5)_3$ has an appreciably stronger alkylating action than the $Al(C_2H_5)_2Cl_2^-$ ion in a solution of $Al(C_2H_5)_2Cl$. This should lead to the acceleration of a type (4) reaction and to the increase of the concentration of $(C_5H_5)_2Ti(C_2H_5)_2$ and thereby to an increase in the rate of the reduction reaction.

The reaction with olefins indicates that one of the species participating in the reaction mechanism must have the ability to add on to an olefin and rearrange itself to form a longer alkyl radical. In our opinion

$(C_5H_5)_2TiC_2H_5^+$ is a radical of this kind. The charge on this radical facilitates the formation of π -complexes with an olefin, which then rearranges to $(C_5H_5)_2TiC_4H_9^+$. In the absence of a strong alkylating agent (as in the case of diethylaluminum chloride) a reaction of this type leads to polymerization. At low ethylene concentrations and in the presence of strong alkylating agents this and the following reactions (4) and (4') lead to the formation of aluminum alkyls containing butyl groups, as in the case of $Al(C_2H_5)_3$ and $(C_5H_5)_2TiCl_2$, and also propyl and butyl groups, as in the reaction of $(C_5H_5)_2TiCl_2$ with $Al(CH_3)_3$ in the presence of ethylene and propylene.

The proposed mechanism can be extended to the reduction of other halides of titanium and also in its main features to the halides of other transitional elements. We would point out that the formation of MeR_2^+ as an intermediate particle [7, 8] has been proposed for the reaction of $RMgX$ with $CoCl_2$ and HgR_2 with VCl_4 , in which the absence of free radicals has also been demonstrated [6, 8].

It may be assumed that catalytic activity in polymerization reactions is due to the formation of $...MeR^+$ ions (Me = transitional element, R = alkyl group) present in solution in the case of homogeneous catalysts and on the surface in the case of heterogeneous catalysts.

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SOME PROBLEMS IN THE THEORY OF THE EXTRACTION OF INNER COMPLEXES

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Consideration of a large amount of data, both from the literature and determined experimentally in our laboratory, permits one to state a number of generalizations concerning the relationship between the extraction of inner complexes (i.c.) and the coordination number of the central atom; these generalizations concern in particular the effect of the nature of the solvent. In the present paper these generalizations are presented briefly and, of necessity, in a schematic manner; they are elucidated in greater detail elsewhere.* The extraction of i.c. is considered in terms of the coordination saturation or unsaturation of the central atom.

The formation of an i.c. is conditional on the forming of one ionic and one coordinate bond between a metal ion and each molecule of an organic reagent. If the coordination number (c.n.) of the metal ion is less than twice the valence, the metal will have no remaining free coordination positions after formation of an i.c., while if the c.n. is more than twice the valence, some of the coordination positions on the central atom will be free. In this connexion i.c. may be split into two groups: 1) i.c. with a coordination unsaturated central atom (we will refer to these as being coordination unsaturated) and 2) i.c. with a coordination saturated central atom (coordination saturated i.c.).

Coordination unsaturated i.c. If a coordination unsaturated i.c. is formed in aqueous solution, the free coordination positions of the metal are found generally to be occupied by water molecules. Thus, for example, Mg forms a complex with 8-hydroxyquinoline in which two water molecules make up the c.n. of magnesium to six. However large and hydrophobic the organic part of the complex, compounds of the type considered cannot generally be extracted. It is clearly possible to make them extractable by two methods. The first method is to eliminate the water molecules. In our view, water may be eliminated by molecules of an organic solvent, by molecules of the organic reagent itself if added in excess, by molecules of another substance present in the system which is capable of coordination, by to complex molecules combining to satisfy their coordination unsaturation (dimerization), by donor atoms present in the complex molecule (other than those already linked to the metal by the formation of the i.c.) satisfying the coordination unsaturation. The second method is to block out the water molecules by molecules of an organic solvent or the reagent, etc., by the formation of hydrogen bonds. In this study we consider the first method. It should be emphasized right away that the possible mechanisms for eliminating water which have been listed above and are considered in greater detail later may be superimposed.

Consider a coordination unsaturated i.c. present in aqueous solution, for example calcium hydroxyquinolate $\text{Ca}(\text{C}_9\text{H}_6\text{NO})_2 \cdot 2\text{H}_2\text{O}$. If there is in addition an oxygen-containing solvent in the system, conditions for competition between molecules of this solvent and water molecules for position in the hydrated and solvated layer surrounding the calcium atom are created. The higher the donor capacity of the organic solvent (or the more polar the solvent), the more it will be favored in this competition. A sufficiently compact structure of the

* Yu. A. Zolotov, and I. P. Alimarin, Collection of Extraction Studies [in Russian] (Moscow, 1961) (at press).

solvent molecule is an essential condition for elimination of water, as steric hinderance will otherwise make coordination of the solvent impossible. If the solvent by virtue of its donor capacity (high polarity) and compact structure replaces water molecules, the compound formed, which is then provided with an even larger organic portion and is deprived of its hydrophilic character, may be able to dissolve in the excess solvent. On the other hand if the solvent used for extraction of the i.c., e.g., C_6H_6 or CCl_4 , is nonpolar and its ability to compete with water molecules is very small, there is only a low probability that the solvent molecules will be able to release the coordinated layer surrounding the calcium from the water molecules, and the hydrated i.c., molecule may be unable to transfer into the organic phase.* In this connection it may be expected that the distribution coefficients obtained when using solvents of low polarity will be lower than for more polar oxygen-containing solvents with well-defined donor properties. Numerous examples can be quoted to show that i.c. of coordination unsaturated ions are extracted by oxygen-containing polar solvents better than by extraction solvents of low polarity which do not contain oxygen.

In many cases the coordination unsaturation of the central atom can be satisfied by the addition of additional neutral reagent molecules to form, say, a compound of the $Me^{IV}R_2 \cdot 2HR$ type. In this case the excess reagent molecules play the same part as an organic solvent. Extraction may take place in this case even when a noncoordinating solvent of low polarity is employed. Which molecules, whether solvent (if a coordinating solvent is employed) or reagent molecules, will actually obtain positions in the coordination envelope depends, as may be expected, on their relative donor capacity, structure and concentration. In many cases anionic complexes of the $Me^{IV}R_2$ type are formed, which may be extracted if their charge is neutralized by the charge or a cation being extracted at the same time.

The extraction of coordination unsaturated i.c. may be achieved by the addition of extraneous substances which are capable of coordination. Such substances could for instance be some coordinating solvents added in small quantity to an inert solvent in order to improve the extraction. They may be some other polar substances, for instance, aliphatic amines [1]. The first author to point out this possibility of improving extraction appears to be Dziomko, who however ascribed a different mechanism to the effect of such substances [2]. Umland and co-workers report systematic studies along these lines [1, 3-8]. The effect of these additives may be twofold. On the one hand there is coordination which has been discussed above, and on the other hand in certain cases the molecules of the added substances are capable of yielding cations which form extractable salts with anionic metallic complexes. For example, in the presence of n-butylamine and excess hydroxyquinoline, calcium is extracted in the form of $C_4H_9NH_2Ca(C_9H_6NO)_2$ [4]. On the other hand Zn and Cd merely form addition products of n-butylamine with a complex of the $Zn(C_9H_6NO)_2 \cdot C_4H_9NH_2$ type (coordination) [5].

Cases where a nonpolar solvent is incapable of displacing water molecules at the central atom, other polar coordinating substances are not present in the solution, but the reagent used cannot be coordinated either due to spatial considerations or because its concentration is not sufficiently high are furthermore not ruled out. The only remaining method of satisfying the coordination unsaturation of the metal in this case is the formation of a bond between neighboring complex molecules, i.e., dimerization in the organic phase. The i.c. molecules themselves thus play the part of the water eliminator. The bond is formed in this case between the central atom and any donor atoms present in a neighboring complex molecule. In this connection the possibility of dimerization will be determined to a considerable extent by the structure of the organic reagent.

Finally it frequently happens that the free coordination positions at the central atom of the i.c. are occupied by donor atoms present in the complex molecule itself (polydentate reagents). In this case the i.c. of coordination unsaturated ions can be extracted even by noncoordinating solvents of low polarity, for example CCl_4 , etc., in the absence of excess reagent and extraneous coordination additives. Thus the dithizonates of a series of coordination unsaturated ions are extracted by CCl_4 . Umland [9] synthesized the tridentate derivative of 8-hydroxyquinoline in order to avoid adding amines to promote the extraction of the hydroxyquinolinates of a series of bivalent metals. The use of polydentate reagents possessing a structure enabling several rings to be formed is, in our view, most promising, the more so as the presence of several rings in the complex increases its stability.

Coordination saturated i.c. Al 8-hydroxyquinolate, Ga pyrocatechinate, the complex of U^{IV} with acetylacetone, and the complex of Pu^{IV} with thenoyltrifluoroacetone may be taken as examples of such compounds. The metal ions in these compounds have no free coordination positions and are well screened by the organic ligands. It

* It is assumed that the reagent molecule does not contain isolated hydrophilic groupings which prevent it from dissolving in organic solvents.

is characteristic of i.c. belonging to this class that the effect of the nature of the solvent on extraction is slight. It does however have some effect even in this case. We will point out two facts which have some significance in this connection.

The old statement that "like dissolves like" appears to be the criterion which determines the choice of solvent in this case. Since the ligand molecules of the i.c. to be extracted do not as a rule contain hydrophilic groups, but are generally simply hydrocarbon chains or rings, the most suitable extraction solvents for the compounds under consideration may prove to be hydrocarbons of low polarity and their halogen-substituted derivatives. On the other hand more hydrophilic and polar solvents containing oxygen prove to be less suitable. Consideration of the interaction between molecules in the solvent itself leads one to the same conclusion. Dyrsen noticed [10] that readily extracted i.c. of the type under consideration are extracted better by nonassociating solvents, in which only weak van der Waals forces act between molecules, as, for instance, in benzene or CCl_4 . If interaction between molecules is enhanced by the introduction of a carbonyl or a hydroxyl group, extraction deteriorates.

It may be assumed that extraction of compounds of the type considered is only slightly dependent on an excess of reagent or the addition of other substances, and also that these compounds have little tendency to dimerize.

In order to use the ideas which have been developed above for practical purposes it is essential to know precisely which ions in the i.c. are capable of exhibiting coordination unsaturation. In considering this problem the fact that the coordination number of an ion does not remain constant in different compounds must be taken into account. It is possible that the nature of the donor atoms to which the ion is attached and the type of compound formed have an effect on coordination number. Coordination unsaturation may be shown by i.c. of Li^+ , Tl^+ , NpO^+ and its analogs, the alkaline earth elements Mn^{2+} , Zn^{2+} , Cd^{2+} , UO_2^{2+} and its analogs. I.c., of tetravalent and, apparently, trivalent elements are coordination unsaturated, although this cannot be asserted definitely with regard to the latter.

The approach to a description of the extraction of i.c. which has been developed above can obviously be used both to interpret earlier experimental data and to give guidance in the choice of solvent and extraction conditions for i.c. the extraction of which has not been investigated. For this purpose it is necessary to assess beforehand the properties: 1) of the metal cation - valence and c.n., occasionally radius, and affinity for the common donor atoms; 2) of the organic reagent - spatial structure, number and location of donor atoms, and presence or otherwise of hydrophilic groups; and 3) of the organic solvent - presence of donor atoms (oxygen) and polarity. On the basis of this information some forecast of the behavior of the element may be made by consideration of the scheme proposed in this paper.

It seems to us to be worthwhile briefly considering, bearing in mind the properties of the metal ion, the numerous recommendations made by a number of previous authors concerning the use of solvents for the extraction of i.c. of elements. These recommendations were based on the assumption that the nature of the extraction solvent did not have much importance. For example, chloroform was recommended for the extraction of all hydroxyquinolinates without exception. One ought to mention that chloroform was sometimes considered a universal solvent for the extraction of i.c.

It is desirable to estimate the capacity of the solvent to coordinate with the central atom when it has displaced the water by some parameter which is convenient to measure or is readily calculated. For oxygen-containing solvents donor capacity is probably a property which is significant in extraction. To express it, the electrical negativity of the oxygen atom for example can be used. A similar approach was used by Berger [11] for complex-forming solvents. However the quantitative expression of oxygen electrical negativity is difficult; even the corresponding series is difficult to obtain. It is possible that for a first approximation it is preferable to employ another property - solvent polarity. This property is all the more convenient as it enables both oxygen-containing and non-oxygen-containing solvents to be assessed on a single basis. Dipole moment, polarizability, dielectric constant, and molar polarization may be used in this case as parameters which are suitable in principle for the comparison of solvents. The two last-mentioned parameters evidently are the most acceptable, but even these cannot of course be used in all cases.

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AN INVESTIGATION OF STERIC EFFECTS IN SOME HALOGEN DERIVATIVES OF NAPHTHALENE

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The problem of the structure of an organic molecule may be divided fairly sharply into two parts. The effect of atoms on each other, which is transmitted along a chain of bonds, leads to a specific distribution of bond lengths. A series of the laws determining bond lengths relevant to aromatic molecules and other cases of conjugated bonds has been established fairly reliably, and a summary of these data can be found in reference [1].

The second structural problem is associated with the effect of atoms which are not involved in valence bonds, which is frequently termed steric effect. A considerable amount of direct and indirect data indicates that these two facets of the problem of structure can in fact be clearly separated. The energy of interaction of atoms involved in valence bonds is greater than that of atoms not involved in valence bonds by one to two factors of ten. The bond lengths are therefore dependent to a very insignificant extent (amounting at any rate to only thousands of an Angstrom unit) on the configuration of the molecule, the strain in the ring, and steric effect.

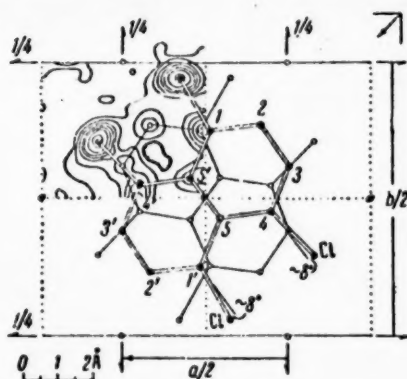


Fig. 1. Structure of 1:4:1':4'-tetrachloronaphthalene. Projection ab.

The fact that interference by the interaction of atoms which are not linked by valence bonds with atoms which are linked by valence bonds is insignificant enables one to formulate the next structural problem: What should the valence angles be in the molecule and what conformation will it adopt at given bond lengths? An approach based on a view of the molecule as a system of electrons and nuclei obeying the laws of quantum mechanics cannot lead to a solution of the given problem. More to the point is a semiempirical approach [2] the essence of which is simply to find the minimum strain energy of the molecule, which is defined as the sum of the energy associated with displacements of the valence angle from its "ideal" value and the energy associated with interactions between all the pairs of atoms which are not linked by valence bonds. It is obvious that information on the stability of the "ideal" angles and on the potential of the interaction of atoms which are not linked by valence bonds is essential for the solution of this problem.

A series of more or less successful attempts along these lines is well known in the literature. If the problem is formulated fairly clearly in the case of aliphatic compounds, for which it is normal to assume that the

displacement, $\Delta\alpha$, of the angle from the "ideal" value is a completely isotropic property, things are a great deal more complicated in the case of aromatics, where interaction of the π -electrons causes a planar disposition of the atoms to be favored. Thus it is possible to describe the energy associated with these angles as the sum of $k\Delta\alpha^2$. Different angular displacements of a bond to the plane of the "ideal" aromatic nucleus undoubtedly possess different energy efficiencies. Any kind of a priori judgements on this score appear to us to be impossible, while certain attempts [3] to deduce the conformations of distorted aromatic systems are considered to be premature.

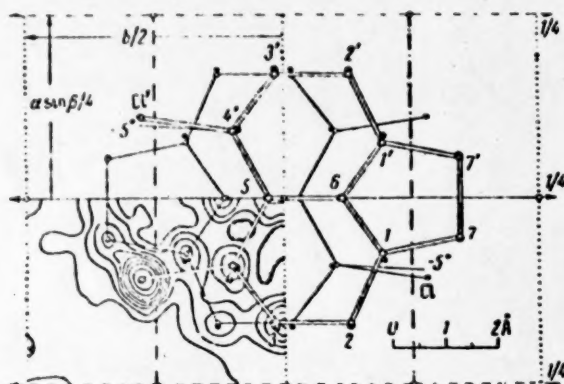


Fig. 2. Structure of 4:4'-dichloroacenaphthene. Projection ab.

In order to make it possible to construct a semiempirical theory, it is necessary initially to study the anisotropy of bond angle displacements in derivatives of aromatic compounds which exhibit steric hindrance. A systematic investigation of this kind has been started in our laboratory. It is proposed in the first instance to study the structure of peri-dihalogen derivatives of naphthalene and later the structure of 4:5-dihalogen derivatives of phenanthrene.

In the present paper we report the first series of experimental results. The structure of the molecules of 1:4:1':4'-tetrachloronaphthalene and 4:4'-dichloroacenaphthene were determined by the techniques of x-ray analysis of crystal structure. The crystals of the first of these compounds belong to the Pccn spatial group with 4 molecules per unit cell, which has the parameters $a = 9.45$; $b = 15.20$; $c = 7.05$ Å. In this case, the molecules are situated in specific positions on the second-order axes (axis 2 is perpendicular to the plane of the naphthalene nucleus). The corresponding data for the other crystal are: spatial group C2/c; $a = 15.38$; $b = 9.45$; $c = 7.48$ Å; $\beta = 118.5^\circ$; 4 molecules in the unit cell, which occupy specific positions on the second-order axes. Study of the structures was carried out by means of electron density projections on the ab boundary (Figs. 1 and 2).

The molecules studied are characterized by considerable steric hindrance effects: in the "ideal" conformations (i.e., with the C-Cl bond lying along the bisector of the valence angle of the C-C-C linkage of the aromatic ring), the Cl...Cl distance is 2.49 Å in the tetrachloronaphthalene molecule and 2.56 Å in the dichloroacenaphthene molecule, which is considerably less than the equilibrium van der Waals distance, which is greater than or equal to 3.7 Å.

The principal result of the study is that due to steric interaction of the atoms the C-Cl bonds are displaced by 8° in the first compound and by 5° in the second from the "ideal" directions (the Cl...Cl distances are then equal to 2.98 Å and 3.12 Å respectively). These displacements occur in the plane of the nuclei, and the displacements in the perpendicular direction (with respect to the normal to the nuclei) are much less and amount to 0.05 and 0.18 Å respectively.

The bond displacements observed are dependent to a overwhelming extent on the interaction of the neutral chlorine atoms (van der Waals interaction, as it is frequently termed). In fact, even taking the most extreme estimates the change of electrostatic energy is ten times smaller than the change in the energy associated with van der Waals interaction at the stated change in the Cl...Cl distance.

The smaller angular displacement in the case of dichloroacenaphthene seems in our view to be completely as expected. As has been shown experimentally [4] and elucidated by calculation [5] the valency angle at atom C_5 in the acenaphthene molecule is increased to 128.4° due to uniform strain distribution over the nucleus. Thus the bisectors of the valence angles of atoms C_4 and C_4' in the acenaphthene molecule itself are already displaced from a parallel position by 3.5° . Therefore the angular displacements of the bisectors in dichloroacenaphthene are approximately 3° less than in tetrachloronaphthalene. The nature of the interaction of the chlorine atoms, which are not linked by valence bonds, is undoubtedly identical in the two compounds studied.

In the ensuing reports we hope to give a quantitative assessment of the stability of the displacement of the C-Cl bond in different directions, commencing with the potential of the interaction of neutral chlorine atoms.

The authors express their indebtedness to V. A. Koptug for supplying the pure compounds required for the study.

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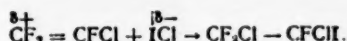
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THE MECHANISM OF THE ADDITION OF IODINE CHLORIDE TO CHLOROTRIFLUOROETHYLENE

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In 1951 Barr and co-workers [1] and in 1952 Haseldine [2] reported that the addition of iodine chloride to trifluorochloroethylene yields a single product, namely 1:2-dichlorododotrifluoroethane. These authors ascribe ionic character to this reaction: The more negatively charged chlorine atom in iodine chloride attaches itself to the positively charged carbon atom of trifluorochloroethylene



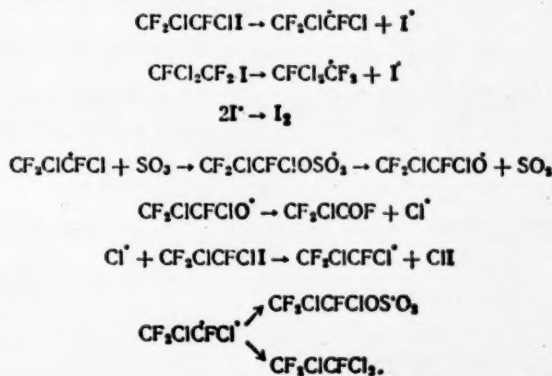
A similar mechanism was observed in connexion with the sequence for the addition of nucleophilic reagents to unsymmetrically substituted fluoro- and fluorochloroolefins.

From the reaction of trifluorochloroethylene with iodine chloride in the conditions described for this reaction by Haseldine, an addition product is formed with a narrow boiling range (53° at 150 mm), which led Haseldine to the erroneous conclusion that it was a single compound. Earlier Bigot [3] had observed the formation of two isomers in the addition of iodine chloride to allyl alcohol.

We have established that the addition product of iodine chloride with chlorotrifluoroethylene is also a mixture of two isomers - 1:2-dichlorododotrifluoroethane ($\text{CF}_2\text{ClCFCII}$) and 1:1-dichloro-2-iodotrifluoroethane ($\text{CFCl}_2\text{CF}_2\text{I}$) in the approximate ratio of 4:1.

When this addition product is treated with oleum a mixture of the fluoroanhydrides of difluorochloroacetic ($\text{CF}_2\text{ClCFCOF}$) and dichlorofluoroacetic (CFCl_2COF) acids, iodine, sulfur dioxide, iodine chloride, and 1:1:2-trichlorotrifluoroethane (Freon 113) is formed.

The reaction with SO_3 has an ionic character

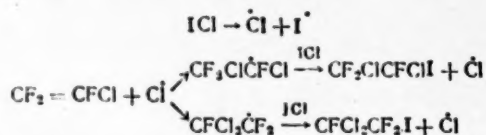


Similarly 1:1-dichloro-2-iodotrifluoroethane on treatment with oleum is converted to the fluoroanhydride of dichlorofluoroacetic acid, while the $\text{CFCl}_2\dot{\text{C}}\text{F}_2$ radical formed in the reaction combined with the F^\cdot radical yields 1:1-dichlorotetrafluoroethane. The formation of two fluoroanhydrides on treatment with oleum can be explained only by the presence of two isomeric addition products $\text{CF}_2\text{ClCFClI}$ and $\text{CFCl}_2\text{CF}_2\text{I}$. The fluoroanhydrides formed yield on reaction with alcohol a mixture of the esters of difluorochloro- and dichlorofluoroacetic acids, which can be easily separated by distillation.

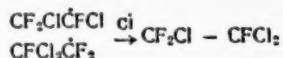
The addition product of iodine chloride and trifluorochloroethylene was used by us previously in the telomerization reaction with tetrafluoroethylene [4]. It is now established that the dichlorodotrifluoroethane distilled from the telomerization products is contaminated with 1:1-dichloro-2-iodotrifluoroethane; this is a consequence of the fact that when oleum acts on the dichlorodotrifluoroethane recovered from the telomerization reaction a mixture of the fluoroanhydrides of difluorochloroacetic and dichlorofluoroacetic acids is formed which contains considerably more of the fluoroanhydride of dichlorofluoroacetic acid than in the oleum treatment of a mixture of isomeric dichlorodotrifluoroethanes which have not participated in a telomerization reaction.

This contamination of one of the isomers cannot be explained by a rearrangement of the CF_2ClCFCl radical to $\text{CFCl}_2\dot{\text{C}}\text{F}_2$ in the conditions of the telomerization reaction as specially run experiments indicate that the ratio of the isomers does not change either when the addition product of iodine chloride and trifluorochloroethylene is heated with benzoyl peroxide in the conditions of the telomerization reaction or on prolonged standing (3 months). Obviously 1:2-dichlorodotrifluoroethane readily forms radicals and participates in the telomerization reaction, as a result of which the dichlorodotrifluoroethane recovered from the telomerization reaction contains more of the second isomer, 1:1-dichloro-2-iodotrifluoroethane, which forms radicals less readily.

On the basis of these facts the possibility cannot be ruled out that the addition of iodine chloride, and possibly many other electrophilic reagents, to chlorotrifluoroethylene proceeds by a free radical and not by an ionic mechanism, as postulated by Haseldine.



The formation of freons also supports a radical mechanism and is the result of the recombination of the CF_2ClCFCl and the $\text{CFCl}_2\dot{\text{C}}\text{F}_2$ with a chlorine or fluorine radical



EXPERIMENTAL

Addition of iodine chloride to chlorotrifluoroethylene. 136 g (0.84 mole) of iodine chloride was placed in a steel flask of 250 ml capacity; the flask was cooled, 81 g (0.7 mole) of chlorotrifluoroethylene was added, and the flask was agitated by a rocking mechanism at 40° for 4 hr. The reaction product was distilled in a column having the equivalent of 17 theoretical plates. Twenty-three g of 1:1:2-trichlorotrifluoroethane, b. p. 47°, and 153 g iododichlorotrifluoroethane, b. p. 53° at 150 mm, n_D^{20} 1.4490, yield 81.5%, were obtained.

Action of oleum on iododichlorotrifluoroethane. 230 ml of 15% oleum was placed in a three-necked flask fitted with a stirrer, dropping funnel and a reflux condenser which was joined by the gas off-take tube to two Drechsel flasks connected in series. 223 g (0.8 mole) of a freshly distilled mixture of the iododichlorotrifluoroethane isomers (b. p. 53° at 150 mm) was added gradually at a bath temperature of 100-102° with stirring.

Gaseous reaction products were absorbed in absolute alcohol in the Drechsel flasks, which were cooled with ice.

On completion of the reaction a dark liquid which proved to be iodine chloride was distilled out of the reaction flask. On cooling, iodine crystallized out in the flask. The alcoholic solution containing the gaseous reaction products was distilled using an efficient dephlegmator, during which sulfur dioxide condensed in the

trap. The alcoholic distillate was poured into ice water; the layer which separated was washed with water, bicarbonate of soda, then again with water, dried with magnesium sulfate and then distilled in a column equivalent to 30 theoretical plates. The following fractions were obtained: 1) b. p. 47-48°, n_D^{20} 1.3590, freon 113; 2) b. p. 95-96° - ethyl ester of difluorochloroacetic acid contaminated with unreacted iododichlorotrifluoroethane; 3) b. p. 131°, n_D^{20} 1.4040, d_4^{20} 1.321 - ethyl ester of dichlorofluoroacetic acid, MR found 32.40; calculated for $C_4H_5FCl_2O_2$ 31.89.

Found %: C 27.52; H 3.15, $C_4H_5FCl_2O_2$. Calculated %: C 27.43; H 2.86.

Fraction 2 was heated for 6 hr with zinc dust at 60-70° and distilled in a column in order to remove contamination by unreacted dichlorodifluoroethane; b. p. 96°, n_D^{20} 1.3572, d_4^{20} 1.253, MR found 27.06, calculated for $C_4H_5F_2ClO_2$ 26.88.

Found %: C 30.42; H 3.37, $C_4H_5F_2ClO_2$. Calculated %: C 30.28; H 3.16.

The product yields are given in the table, based on 223 g (0.8 mole) of iododichlorotrifluoroethane.

Iododichlorotrifluoroethane, 223 g (0.8 mole)	$CFCl_2-CF_2Cl$		$CF_2ClCOOC_2H_5$		$CFCl_2COOC_2H_5$	
	g	%	g	%	g	%
Freshly distilled	5.5	4	66	52	18	13
Room temperature for three months	16.2	11	65	51	20	14
Heated for 4 hr at 110° in the presence of 1% benzoyl peroxide	10.2	7	64	50	16	11
Recovered from telomerization reaction with tetrafluoroethylene	12.5	8	39	30	44	31

The initial iododichlorotrifluoroethane was distilled in a column equivalent to 17 theoretical plates prior to the reaction; b. p. 53° at 150 mm, n_D^{20} 1.4492.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

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SYNTHESIS OF K-STROPHANTHIN-8

Corresponding Member Academy of Sciences USSR

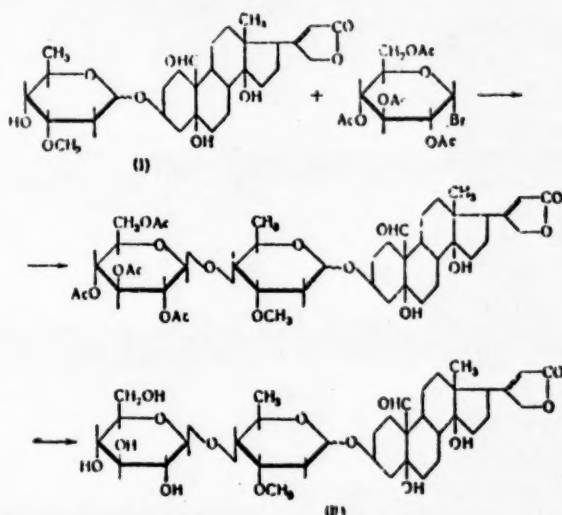
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Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 3, pp. 613-616,
January, 1961

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Among a large group of cardiac glycosides for practical medicine the glycosides of various species of *Strophanthus* are of great significance. Ranking high among these is the bioside K-strophanthin-8, which was isolated for the first time in pure form by Jacobson [1], and for which the structure 4- β -glucosyl-D-cymaroside strophanthidin (II) was established. Due to the difficulties connected with isolation of K-strophanthin-8 from natural substances, which are not always available, the partial synthesis of this important glycoside from more available natural raw products, namely the available cymarol monoside (D-cymaroside strophanthidin), is of interest. In the present article the preliminary data for this synthesis are presented.

In the literature several methods of synthesis of monosides containing cardiac aglycons have been described [2-7]. However, we were unable to find any mention of attempts to synthesize biosides, particularly the most important of these, K-strophanthin-8. Since in cymarol (I) the carbohydrate residue of cymarose contains the only free hydroxyl group, tertiary hydroxyl groups are of low reactivity toward hydrogen-substitution reactions, and the glucose-cymarose linkage in K-strophanthin-8 has the β configuration, it would seem possible to synthesize this bioside according to the Koenigs-Knoor method, with subsequent removal of the acetyl groups by some sufficiently gentle method.



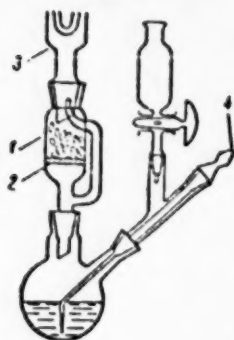


Fig. 1. Reaction apparatus: 1) metallic sodium; 2) porous glass plate; 3) reverse condenser; 4) nitrogen lead-in.

Due to the high lability of the glucoside linkage in cymarín as glucoside 2-deoxysucrose and its aglycon portion, the entire synthesis required careful selection of reaction conditions and control of the course of reaction. Preliminary experiments on condensation of tetraacetylglucosylbromide with cymarín in the usual conditions of the Koenigs-Knorr synthesis, i.e., in the presence of silver carbonate in benzene-dioxane solution, either gave negative results or led to formation of only traces of bioside. Examination of the condensation conditions showed that the failure was apparently due to the presence of water, which was formed as a result of interaction of HBr with Ag_2CO_3 in the reaction mixture. Therefore there arose the necessity of selection of an effective method of removal of water from the reaction mixture. Application of the usual drying agents (MgSO_4 and others) to the Koenigs-Knorr synthesis as well as the attempt of continuous distillation of water in vacuum in a stream of nitrogen did not lead to the desired results. Application of the known method of azeotropic distillation required considerable dilution of the reaction mixture, which led to almost complete cessation of the reaction. In order to eliminate this difficulty, we carried out the reaction in a special apparatus (Fig. 1) where the water was continuously distilled off with benzene and completely taken up by the metallic sodium. This allowed the process to proceed in a sufficiently concentrated solution at constant volume of the reaction mixture.

The analysis of the reaction mixture by paper chromatography showed that at these conditions a considerable amount of substance was formed corresponding, according to R_f , to K-strophanthin-8. Simultaneously, there remained in the reaction mixture a considerable amount of the initial cymarín, which was retained even if an excess of acetobromoglucose was used and the reaction duration was increased. Moreover, some new substance was formed, possessing, judging from the paper chromatography data, high polarity.

The reaction product prepared by the above-mentioned method, isolated in impure form, was deacetylated by the action of KHCO_3 in water-methanol solution with subsequent purification by extraction, chromatography, repeated extraction, and recrystallization.

The pure product did not differ from the sample of natural K-strophanthin-8 in its melting point, color reactions, and biological activity. It was homogeneous and identical with the established natural sample* in the three systems. The presence of the glucose residue linkage was proved by hydrolysis, after which glucose was identified by chromatographic means and by the color reaction with antron in the hydrolyzate [8]. The absence of changes in the aglycon molecule, which may have been expected due to the lability of strophanthidin, was shown by a positive Legale reaction, pointing out the butenolid cycle, and by the u.v. spectrum, which had the maxima characteristic of the butenolid cycle (λ_{max} 223 m μ , $\log \epsilon = 4.119$) and of the C_{15} aldehyde group (λ_{max} 306 m μ , $\log \epsilon = 1.715$). Moreover, the identity of the prepared product with K-strophanthin-8 was proven by the comparison of the i.r. spectra (Fig. 2). At our disposal were two samples of K-strophanthin-8 obtained from different sources. The i.r. spectrum of our product was completely identical with the i.r. spectrum of one of these and showed a shift of the maximum corresponding to the valency shift of the $\text{C}=\text{O}$ group of butenolid cycle 15 cm^{-1} in the direction of the lower frequencies as compared to the corresponding maximum of the other sample of K-strophanthin-8 (1744 and 1759 cm^{-1} respectively).

EXPERIMENTAL

All the solvents used, unless mentioned otherwise, were distilled. Evaporation of solutions in all cases was carried out in a vacuum in a nitrogen current at a temperature not exceeding 40° .

Paper chromatography. Descending, Schleicher and Shul paper, System I: n-butanol-toluene-water (1:1:1), the upper layer. The paper was impregnated by 25% solution of water in methanol. System II: chloroform-n-butanol-ethanol (100:4:1). The paper was impregnated with a 15% solution of formamide in methanol. System III: n-butanol saturated with water. Staining of spots was carried out by means of an alkaline water-alcohol solution of sodium picrate.

*The authors consider it a pleasant duty to express this sincere gratitude to Prof. Bauer (Slavic Academy of Sciences) for a sample of pure K-strophanthin-8.

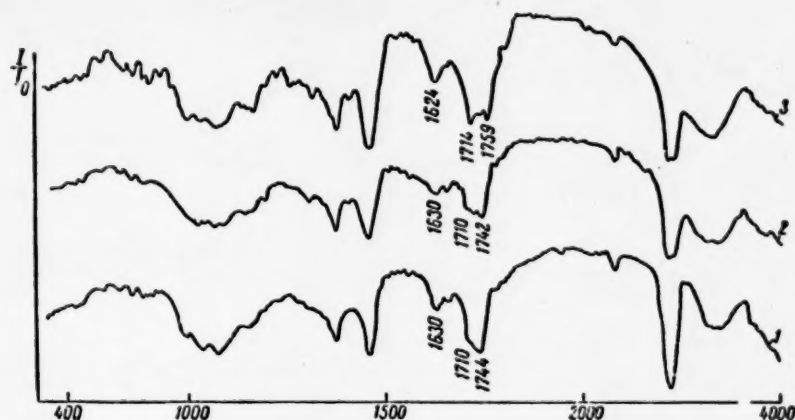


Fig. 2. I.r. absorption spectra in paraffin oil. 1) Synthetic K-strophanthin-B; 2,3) first and second samples of natural K-strophanthin-B. 1710 and 1714 cm^{-1} , C_{19} C=O group valence shifts; 1744, 1742 and 1759 cm^{-1} , C=O group valence shifts of butenolid cycle; 1630 and 1624 cm^{-1} , C=C group valence shifts of butenolid cycle.

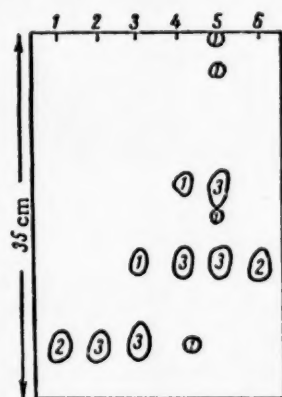


Fig. 3. The chromatogram of the reaction mixture after distribution. System I. 1) Cymarin; 2) CHCl_3 - extract; 3) CHCl_3 - alcohol (9:1) - extract; 4) CHCl_3 - alcohol (4:1) - extract; 5) CHCl_3 - alcohol (3:2) - extract; 6) K-strophanthin-B. The color intensity of the spots was evaluated by means of a three-point system (number within spots).

Starting materials. Cymarin: The commercial product was recrystallized twice from methanol, dried in a vacuum at 100° ; m. p. $147-150^\circ$. Acetobromoglucose: m. p. $88-89^\circ$; $[\alpha]_D + 205^\circ$ (CHCl_3). Silver carbonate. The freshly precipitated salt was carefully washed with water and ethanol. It was dried in vacuum over P_2O_5 and immediately introduced into the reaction.

Synthesis of K-strophanthin-B. Into a round-bottom flask apparatus (Fig. 1) 721 mg (1.3 mM) of cymarin and 6 ml of absolute benzene were placed. The mixture was heated in a current of dry, oxygen-free nitrogen at a bath temperature of $105 \pm 2^\circ$. To the mixture, 4.5 g (16.5 mM) of silver carbonate and a solution of 2.5 g (6.1 mM) acetobromoglucose in 3.75 ml of absolute dioxane were added in the following sequence (the intervals of time, starting from the time of heating, are indicated): 2 hr, 2.0 g Ag_2CO_3 ; 2 hr 30 min, 3 ml acetobromoglucose solution; 2 hr 50 min, 1.5 g Ag_2CO_3 + 0.75 ml acetobromoglucose solution; 4 hr 50 min, 1.0 g Ag_2CO_3 ; 7 hr 10 min, 1.0 g Ag_2CO_3 ; 8 hr 40 min, the mixture was cooled with a stream of nitrogen, filtered, the residue washed with dioxane, chloroform and methanol, and the filtrate evaporated to dryness. The residue was dissolved in 200 ml of methanol, and a solution of 7 g of potassium bicarbonate in 150 ml of water was added. The mixture was left to stand for 7 days and filtered, and the filtrate was evaporated to half its volume. The aqueous solution obtained was consecutively extracted with chloroform (400 ml), mixtures of chloroform and alcohol 9:1 (400 ml), 4:1 (400 ml) and 3:2 (700 ml) (for example cf. [5]). The extracts were evaporated to dryness and dried in vacuum at $60-80^\circ$. Thus we obtained: from a chloroform extract a yellow powder, weight 225 mg (regenerated cymarin); from a 9:1 chloroform - alcohol extract a yellow powder, weight 43 mg; from 4:1 a yellow powder, weight 97 mg; from 3:2 a yellow powder, weight 230 mg.

The prepared products were analyzed by means of paper chromatography (Fig. 3).

Chloroform-alcohol (4:1) extract (85 mg) was subjected to partition chromatography on cellulose in a system CHCl_3 -alcohol/ H_2O with gradient elution. The column had a 5.6-cm^2 cross section; the height of the

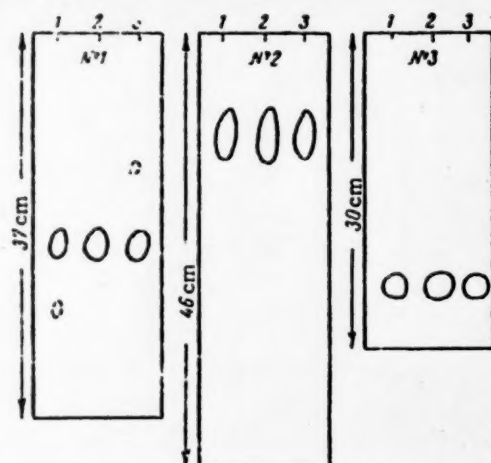


Fig. 4. Chromatogram of the pure synthetic K-strophanthin-B: No. 1, system I; No. 2, system II; No. 3, system III. 1,3) First and second samples of natural K-strophanthin-B; 2) synthetic product.

adsorbent column was 34 cm. The cellulose was saturated with water vapor at 25°, and the column was packed by a saturation method in 5% solution of alcohol in chloroform. The volume of the solvents in the mixture was 400 ml, with an alcohol concentration 5%. 20% solution of alcohol in chloroform was added. After 250 ml of blank fractions from the column, 150 ml of solution was obtained containing 50 mg of K-strophanthin-B with a negligible admixture of cymarín. Then the fractions containing the more polar components of the mixture were collected. The K-strophanthin-B thus obtained was dissolved in 25 ml H₂O and the solution filtered and extracted successively with CHCl₃, 100 ml; CHCl₃-alcohol (20:1) 70 ml; and CHCl₃-alcohol (2:1), 100 ml. The final extract was evaporated to dryness and dried in vacuum. A colorless powder, weight 25 mg. The product was reprecipitated in ether from alcohol and dried at 100° (10⁻⁵ mm). M. p. 180-196° (decomposition).

The substance was chromatographically homogeneous and identical with the known samples (Fig. 4). It gave positive reaction with antron, positive Legale reaction, and a green color with H₂SO₄.

Found %: C 58.80, 58.98; H 7.54, 7.36. C₃₆H₅₄O₁₄ · H₂O. Calculated %: C 59.32; H 7.74.

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CHEMICAL INVESTIGATION OF A NEW CARDIAC GLYCOSIDE
FROM ERYSIMUM CHEIRANTHOIDES L.*

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(Presented by Academician A. I. Oparin, August 18, 1960)

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By the method of paper chromatography, 12 substances, which must be regarded as cardiac glycosides and aglycons (cf. figure) were found to be present in the grass of *Erysimum cheiranthoides* L.

To isolate the glycosides, the crushed grass was extracted with 96% alcohol. On evaporation of the solvent in vacuum, the extracted matter was treated with water and purified with ether, then treated with $Pb(OH)_2$. The glycosides were extracted from the aqueous solution with a 2:1 mixture of chloroform and alcohol. On evaporation of the solvent the residue was redissolved in a small quantity of water and treated as before with a 2:1 mixture of chloroform with alcohol. The total quantity of glycosides obtained after condensation of the alcohol-chloroform extracts was chromatographed on aluminum oxide. Development was carried out with chloroform and then with chloroform-alcohol mixtures in which the alcohol content was gradually increased. The operation of the column was controlled by paper chromatography tests. Eluates containing individual substances were collected separately. By applying this method, we were able to separate 4 substances in their specific crystalline form. The physicochemical properties of these substances are given in Table 1.

The first two substances were identified as the already known aglycon strophanthidin and the known glycoside erysimotoxin [1]. The remaining two proved to be new *Erysimum cheiranthoides* glycosides which were found to have a strong physiological activity, according to data obtained in the pharmacological laboratory. We named the two new substances glycoside I and glycoside L.

The chemical investigation of glycoside I forms the subject of the present communication. Glycoside I was found to crystallize in colorless needles from acetone-ether. The yield of crystalline substance was 0.025-0.03% with reference to the dry raw material. The glycoside is readily soluble in water and alcohol and soluble sparingly in benzene and chloroform. It gives all reactions that are characteristic for cardiac glycosides with a five-membered lactone ring: Legal's, Raymond's, and Kedde's. With Keller-Killiani's reagent it gives a dark-green coloration. It dissolves in 84% sulfuric acid with a green coloration which in 15 min changes to orange and in 2 hr to yellow.

The absorption spectrum of the glycoside in ultraviolet showed two maxima: one at 220 m μ ($\log \epsilon = 4.15$), which indicates the presence of a five-membered lactone ring, and another at 305 m μ ($\log \epsilon = 1.49$), which corresponds to the aldehyde group at C₁₀. The glycoside was analyzed after being dried for 3 hr at 80° in high vacuum.

Found %: C 59.76; H 7.63. $C_{34}H_{50}O_{13} \cdot H_2O$. Calculated %: C 59.63; H 7.65.

Mol. weight: found 684.3, calculated 684.79.

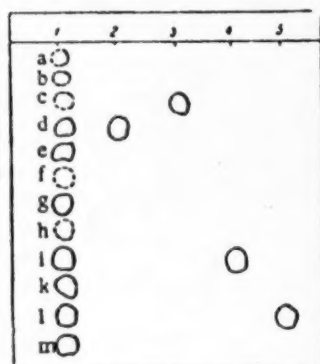
To elucidate its chemical constitution, glycoside I was subjected to stepwise hydrolysis. As a result of the action of the enzyme of pancreatic juice of the snail, it was split into a pentose and a monoglycoside.

* From a dissertation by I. F. Makarevich.

TABLE 1

Properties of Glycosides and Aglycones of *Erysimum cheiranthoides* L.

Name of substance	Mol. wt. and empirical formula	M.p., °C	$[\alpha]_D$	R_f	Physiological activity in mg/kg of the wt. of a cat
Strophanthidin	405,0 $C_{23}H_{32}O_8$	232—233	+46,0° (ethanol)	0,11	0,33
Erysimotoxin	534,7 $C_{23}H_{32}O_8$	194—195	+28,6° (ethanol)	0,18	0,095
Glycoside I	684,3 $C_{31}H_{44}O_{11} \cdot H_2O$	229—230	+17,1° (ethanol)	0,55	0,11
Glycoside L		189—190	-25,3° (ethanol)	0,74	0,12



Chromatogram of cardiac glycosides and aglycons of *Erysimum cheiranthoides* L. on paper No. 2, M from the Volodarskii Plant at Leningrad with the solvent combination chloroform-isoamyl alcohol - water (1:1:1); mobile phase: water saturated with organic solvents; 20°; 24 hr. 1) Purified extract of *Erysimum cheiranthoides* L. grass; 2) erysimotoxin; 3) strophanthidin; 4) glycoside I; 5) glycoside L. Values of R_f : a) 0,02; b) 0,05; c) 0,11; d) 0,18; e) 0,27; f) 0,35; g) 0,45; h) 0,51; i) 0,55; k) 0,67; l) 0,74; m) 0,87.

In 84% sulfuric acid the glycoside dissolved with a brown coloration which changed to green and then to blue.

Found %: C 65,02; H 8,06. $C_{29}H_{42}O_9$. Calculated %: C 65,15; H 7,92.

Mol. weight: found 534,3; calculated 534,65.

Acidic hydrolysis of the monoglycoside takes place easily with the splitting off of one molecule of 2-des-oxy sugar. When an 0,2 N H_2SO_4 solution was used at room temperature, the crystallization of the aglycon in the form of rhombic prisms began already at the expiration of 1,5 hr. On recrystallization from alcohol, the aglycon had a m. p. = 176-177°; on being recrystallized from chloroform-benzene, it had a m. p. = 232-233°; $[\alpha]_D^{25} = +46,1^\circ$ (ethanol, c = 0,94).

The sugar component that has been split off vigorously reduces Fehling's reagent, cannot be fermented with yeast, and readily forms furfural on being heated with hydrochloric acid. The furfural that has formed yields with phloroglucinol a black-green precipitate of furfural phloroglucide, which is insoluble in alcohol; this is a characteristic reaction whereby pentoses are distinguished from methylpentoses.

On being chromatographed on paper with the use of different solvent combinations, the sugar gave R_f values identical with those of d-xylose. The sugar was found to crystallize readily from an alcohol-ether solution in the form of prisms with a m. p. = 145-147°; $[\alpha]_D^{25} = +18,4^\circ$ (aqueous solution, after 2 hr, c = 0,71). In a sample mixed with authentic d-xylose the sugar derived from the glycoside I did not give a melting point depression. The osazone prepared from this sugar was in the form of yellow needle-shaped crystals with a m. p. = 162-163°. A sample mixed with the osazone of authentic d-xylose had the same melting point.

As far as its properties are concerned, the sugar obtained on enzymatic hydrolysis of glycoside I proved to be identical with d-xylose. The presence of pentoses in cardiac glycosides is a rather rare phenomenon. After d-xylose has been split off from glycoside I, a monoglycoside is obtained which crystallizes from methanol in the form of long spear-shaped platelets with a m. p. = 194-195°; $[\alpha]_D^{25} = +28,2^\circ$ (ethanol, c = 1,05).

The monoglycoside was also found to give all reactions that are characteristic for cardiac glycosides with a five-membered ring. A positive Keller-Kiliani reaction (blue coloration) indicated that the glycoside in question contains a 2-des-oxy sugar.

The aglycon was found to be soluble in alcohol and chloroform, less soluble in benzene, and very little soluble in water. It gave positive Legal and Liebermann reactions and a negative Keller-Killiani reaction. It dissolved in 84% H_2SO_4 with a yellow-green coloration which changed to orange and then to green.

Found %: C 68.07; H 7.91. $C_{23}H_{32}O_6$. Calculated %: C 68.29; H 7.97.

Mol. weight: found 405.0; calculated 404.51.

Authentic strophanthidin and a mixture of strophanthidin with the aglycon from glycoside I had the same melting point. In paper chromatography with the use of different combinations of solvents these two aglycons were found to behave alike. The glycoside I aglycon, just like strophanthidin, gave a monoacetyl derivative which crystallized from methanol in the form of colorless prisms with a m. p. = 242-243°; $[\alpha]_D^{25} = +53.2^\circ$ (ethanol, $c = 1.00$).

Found %: C 67.29; H 7.71. $C_{25}H_{34}O_7$. Calculated %: C 67.24; H 7.67.

Mol. weight: found 447.01; calculated 446.54.

It follows from what has been said above that the aglycon of glycoside I is in every respect identical with strophanthidin.

After separation of the aglycon from the acid hydrolyzate, the latter yielded a crystalline 2-desoxysugar which melted at 109-100°. On the basis of paper chromatography and determination of the physicochemical properties, this sugar was found to be identical with d-digitoxose.

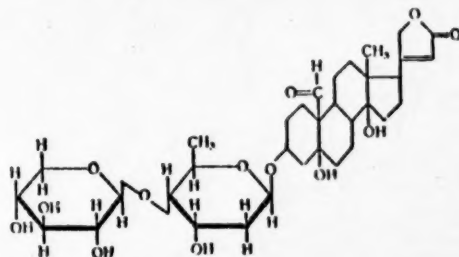
Comparison of the molecular rotations of glycoside I ($[M]_D = +177$), the monoglycoside ($[M]_D = +150.6$), and the aglycon ($[M]_D = +186.7$) according to Klyne's rule [2] indicated that both the digitoxose and the xylose are attached by beta-glycoside bonds (see Table 2).

TABLE 2

Comparison of Molecular Rotations of the Methylglycopyranosides of d-Digitoxose and d-Xylose with the Molecular Rotations of These Sugars in Glycoside I

Sugar	$[M]_D$ of methylglycopyranosides		Molecular rotation of the sugar components in glycoside I, ΔC	Configuration of sugars in glycoside I
	α	β		
d-Digitoxose	+311	+60 [3]	-36.1	β
d-Xylose	+252.7	-108.5 [5]	-33.6	β

Thus, glycoside I is strophanthidin beta-d-digitoxoso-beta-d-xyloside [3]. Its structure can be expressed by the following most probable formula:



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NEW COMPLEX COMPOUNDS OF THE HEXAFLUORIDES OF MOLYBDENUM, TUNGSTEN, AND URANIUM WITH THE FLUORIDES OF CESIUM AND AMMONIUM

N. S. Nikolaev and V. F. Sukhoverkhov

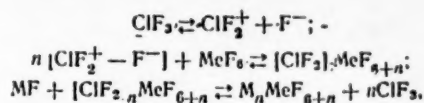
(Presented by Academician I. V. Tananaev, September 19, 1960)

Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 3, pp. 621-623, January, 1961

Original article submitted June 4, 1960

The interaction of the hexafluorides of tungsten, molybdenum, and uranium with the fluorides of alkali metals and of ammonium was first reported by O. Ruff and co-workers [1-3]. However, these authors did not describe the double compounds which form in this interaction; they merely stated that reduction of uranium takes place as a result of the action of gaseous ammonia. Martin, Albers, Dust, and others [4-7] synthesized a number of complex compounds that are formed by uranium hexafluoride with the fluorides of potassium, sodium, rubidium, and silver, viz., K_3UF_9 , Na_3UF_9 , Ag_3UF_9 , and Rb_2UF_8 . On the basis of the work mentioned above, Cox and Sharp [8] prepared complex compounds with the general formulas M_2MoF_8 and M_2WF_8 (where $M = Na, K, Rb, Cs$) from Mo and W hexafluorides and hexafluorides of alkali metals. The principal method of synthesizing compounds of this class was by a reaction of the adsorption type between the gaseous hexafluorides and the alkali metal fluorides. Hargreaves and Peacock [9, 10] reported that the interaction of molybdenum and tungsten hexafluorides with the fluorides of alkali metals in iodine pentafluoride solutions yielded heptafluorotungstates and heptafluoromolybdates of rubidium and cesium in addition to salts of the general formula M_2MeF_8 . However, these authors apparently did not succeed in isolating the salts in question in a pure state, as can be seen from the analytical data reported by them.

The present communication deals with the synthesis of complex compounds of the general formula $MMeF_7$ that are formed by molybdenum, tungsten, and uranium hexafluorides with the fluorides of cesium and ammonium. For the synthesis of these compounds, a basically new method was used that involved the interaction of Mo, W, and U hexafluorides with the fluorides of alkali metals in chlorine trifluoride solutions according to the following tentative scheme:



where $Me = Mo, W, U$; $M =$ alkali metal.

The equilibrium relating to the dissociation of chlorine trifluoride had been determined earlier [11]. The solubilities of the individual components in chlorine trifluoride, which were determined by us at 0°, proved to be MoF_6 95.1 ± 0.5% ; WF_6 99 ± 1% ; UF_6 49.13 ± 0.3% ; CsF 16.05 ± 0.4%. The solubility of uranium hexafluoride in chlorine trifluoride that was found corresponds to the solubility calculated theoretically on the basis of Raoult's law [12]. The solubility of ammonium fluoride in ClF_3 could not be determined because of the rapid combustion of this salt. This combustion may acquire the characteristics of an explosion. The solubilities of other alkali metal fluorides were found to be very low.

Compound	F, wt. %		Cs, wt. %		NH ₄ , wt. %		Mo, wt. %		W, wt. %		U, wt. %		Color
	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	found	calcd.	
Cs(MoF ₇)	37.0 ± 0.5	26.754	36.0 ± 0.3	36.729			26.07 ± 0.3	26.515	41 ± 0.4	40.886	47.35 ± 0.2	47.237	White
Cs(WF ₇)	30 ± 0.5	28.546	28.7 ± 0.3	29.546									White
Cs(UF ₇)	26.32 ± 0.5	26.389	26.4 ± 0.4	26.372									Yellow
NH ₄ (MoF ₇)	53.45 ± 0.5	53.848			7.15 ± 0.5	7.303	39.2 ± 0.1	38.847					White
NH ₄ (WF ₇)	40.1 ± 0.6	39.705			5.5 ± 0.1	5.385			55.1 ± 0.2	54.908			White
NH ₄ (UF ₇)	34.57 ± 0.2	34.180			4.83 ± 0.2	4.636					61.11 ± 0.2	61.183	Yellow

* Prepared for the first time.

The reactions investigated were carried out in 100-ml teflon vessels by combining the reacting solutions in quantities sufficient to bring about formation of 30-40 g of salt. The homogeneous nature of the reaction and the absence of extraneous reactions such as reduction or hydrolysis in chlorine trifluoride solutions were factors ensuring the purity of the resulting products.

The hexafluorides used were prepared by fluorinating the metals with gaseous chlorine trifluoride. As a result of the reactions between solutions of MoF₆, WF₆, and UF₆ and the solution of cesium fluoride, precipitates formed which were soluble with difficulty in an excess of chlorine trifluoride. This made it possible to wash the precipitates with chlorine trifluoride. After this washing the remaining traces of chlorine trifluoride were removed by using vacuum; in this manner, pure salts were obtained which did not contain the initial reacting substances.

Because of the decomposition of ammonium fluoride in chlorine trifluoride, a different method was used for the synthesis of ammonium salts. Dry NH₄F was added in small quantities to saturated solutions of Mo, W, and U hexafluorides in ClF₃, with cooling of these solutions with solid carbon dioxide. The NH₄F had to be added with especial care because of the possibility of decomposition of this salt. The crystals which precipitated were broken up and subjected to additional treatment with hexafluoride solution, whereupon washing with chlorine trifluoride was carried out 3 times and evacuation with cooling applied. The cooling was necessary to prevent reduction.

The isolated salts were subjected to a complete chemical analysis. The fluorine content was determined by titration with an aluminum chloride solution. Cesium was determined gravimetrically in the form of Cs[CO(NO₂)₆]·H₂O, ammonia by distillation from concentrated caustic alkali followed by titration with acid. Both volumetric and gravimetric methods were used for the determination of molybdenum, tungsten, and uranium; the metals were determined as oxides and by precipitation with o-hydroxyquinoline. The results of the analytical determinations are shown in the table.

It is worth noting that in the compounds synthesized the very rare coordination number 7 is encountered. This is in accordance with O'Brien's ideas on the subject, who is of the opinion that halogens in general, and fluorine in particular, enhance the tendency toward the formation of compounds with this coordination number [13].

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INVESTIGATION OF THE KINETICS OF DIRECT REPLACEMENT
OF THE NITROGROUP WITH CHLORINE IN NITROBENZENE
AND *m*-CHLORONITROBENZENE UPON ACTION OF CARBON
TETRACHLORIDE ON THEM

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(Presented by Academician A. V. Topchlev, July 2, 1960)

Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 3, pp. 624-627,

January, 1961

Original article submitted July 2, 1960

Nitrocompounds, particularly aromatic nitrocompounds, have been investigated thoroughly [1]; because of their accessibility, they are used extensively as initial materials for the synthesis of different organic compounds. We are investigating the preparation of aromatic halogen-substituted compounds from nitrocompounds by the direct substitution of the nitrogroup with halogen. We have proposed a number of novel reagents, including CCl_4 , for the direct replacement of nitrogroups with chlorine [2-5]. Carbon tetrachloride has a high chlorine content (92.2%) and possesses a number of other advantages as compared with the most commonly used reagent, PCl_5 .

Because direct replacement of the nitrogroup with chlorine by means of CCl_4 may find extensive application both in laboratories and in technology, we have investigated the kinetics of the reaction of some nitrocompounds with CCl_4 . We used nitrobenzene and *m*-chloronitrobenzene as nitrocompounds.

The kinetics of the reaction of CCl_4 with these nitrocompounds were investigated on a thermophotometer devised by A. A. Ponomarenko, which was called by us earlier a thermophotocolorimeter [6]. This device makes it possible to measure during the course of the reaction the intensity of light absorption in the visible region of the spectrum by a sealed glass tube containing the reacting substances.

We established that as a result of the reaction of CCl_4 with aromatic nitrocompounds NO_2 , NO , NOCl , COCl_2 , CO , CO_2 , H_2O , aromatic compounds containing chlorine, and some other substances are formed as intermediate or final products. After the reaction of CCl_4 with nitrobenzene, chlorobenzene was obtained with a yield amounting to 82% of the theoretical and also a small quantity of dichlorobenzene. *m*-Dichlorobenzene was obtained from *m*-chloronitrobenzene with a yield amounting to 92% of the theoretical.

Among all the substances mentioned only NO_2 and NOCl are colored. The first compound is formed in the very beginning of the process of conversion, the second at its end. The process of substitution of the nitrogroup with chlorine is accompanied by an appearance, accumulation, and decrease of the quantity of NO_2 in the tube during the course of the reaction.

Reaction of CCl_4 with $\text{C}_6\text{H}_5\text{NO}_2$. The reacting substances were combined in quantities of 0.0337 g of $\text{C}_6\text{H}_5\text{NO}_2$ and 0.0840 g of CCl_4 (1:2) per 1 ml of the volume of the tube (v = approx. 6.2 ml). The sealed tubes were placed in the thermophotometer, which was set for the required temperature. Figure 1 gives a curve expressing the dependence of the reaction velocity on the temperature, which shows that at 250° (curve 1) the reaction accompanied by the formation of nitrogen dioxide began after the passage of 17 min. The light absorption (I in %) increased rather rapidly, reaching a maximum at the 38-min point. After this, the value of I

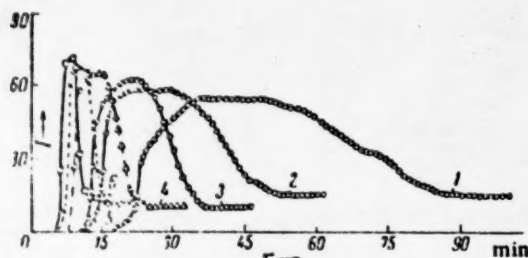


Fig. 1. Dependence of the velocity of the reaction of CCl_4 with nitrobenzene on the temperature. 1) 250° ; 2) 260° ; 3) 270° ; 4) 280° ; 5) 290° ; 6) 300° .

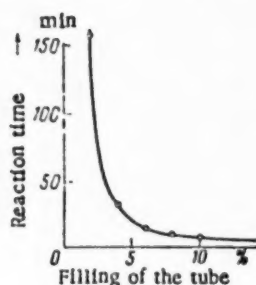


Fig. 2. Dependence of the time required for the reaction of CCl_4 with nitrobenzene on the degree of filling of the tube with the reacting substances. The reaction was carried out at 290° .

remained practically constant for 15 min and then slowly decreased for 38 min. At the 87th minute, the value of I reached a minimum. At this point, as has been found in special experiments, the conversion of the nitrocompound into the chlorocompound is practically at its end. Seventy minutes passed from the moment when the evolution of NO_2 began until the end of the reaction. At the temperatures of 260° , 270° , 280° , 290° , and 300° the reaction was found to begin earlier — within 12, 10, 8, 6, and 5 min, respectively — and to end sooner, viz. in 40, 27, 17, 11, and 7 min. The values of the temperature coefficient of the reaction (250 – 300°) that had been measured varied within the limits of 1.48–1.75. An increase of the temperature from 250° to 300° led to an increase in the reaction velocity by a factor of 10.

The activation energy for the reaction between nitrobenzene and CCl_4 was calculated starting from Arrhenius's equation [8, 9]:

$$\ln \frac{k_1}{k_2} = \frac{Q}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

If we substitute in this equation k_1/k_2 with t_2/t_1 , where t_1 and t_2 are the periods of time within which 40% of light absorption by the tubes at the temperatures of 270° and 280° is achieved (the time was measured from the moment when the value of I began to increase to the point when the required percentage of light absorption was reached at the end of the substitution process), we find that the over-all activation energy of the complex reaction taking place between nitrobenzene and CCl_4 equals 34.5 kcal/mole.

The dependence of the velocity of the reaction between nitrobenzene and CCl_4 on the degree of filling of the tube with the reacting substances can be seen from Fig. 2. When the tubes were filled with a 1:2 mixture of nitrobenzene with CCl_4 to the extent of 2, 4, 6, 8, and 10% of the tubes' volume capacity, the time required for the reaction was 157, 33, 14, 10, and 7 min, respectively. An increase of the degree of filling of the tube from 2% to 10% resulted in an increase of the reaction velocity by a factor of 22.4. These data show that the velocity of the reaction between the compounds investigated depends to a considerable extent on the pressure.

From the quantities of the initially used reacting substances, the approximate pressure in the tubes at the moment when evolution of NO_2 began could be calculated. It was found that at a 2% filling of the tube the pressure must be approximately 12 atm. At a filling of 4% it would be approximately 18 atm and at one of 6%, 23 atm.

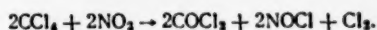
Reaction of CCl_4 with $m\text{-C}_6\text{H}_4\text{ClNO}_2$. The reacting substances were combined in quantities of 0.0430 g of m -chloronitrobenzene and 0.0840 g of CCl_4 (1:2) per 1 ml of the capacity of the tube. The reaction was conducted at the temperatures of 260° , 270° , and 280° . The time required for the reaction at these temperatures was found to be 52, 30, and 22 min, respectively. The temperature coefficients of the reaction for the ranges of 260 – 270° and 270 – 280° were found equal to 1.73 and 1.36. The over-all activation energy was found to be 23.5 kcal/mole.

The reactions of nitrobenzene, m-chloronitrobenzene, and p-chloronitrobenzene with CCl_4 proceed similarly. To interpret the mechanism of the reaction of the first two compounds with CCl_4 , we will cite data obtained by investigating the reaction of NOCl and COCl_2 with p-chloronitrobenzene, and also of NO_2 with CCl_4 .

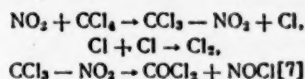
Reaction of CCl_4 with NO_2 . Into a tube having a capacity of 6.8 ml, 0.0592 g of NO_2 and 0.2652 g of CCl_4 were placed. On heating of the tube in the thermophotometer for 276 min at temperatures from 14 to 290°, the following changes in light absorption were observed:

τ , min	0	15	30	40	60	70	90	110	130	150	180	200	276
t , °C	14	51	138	186	246	269	290	290	290	290	290	290	290
I , %	0	33	84	85	85	83	81	75	64	43	21	20	25

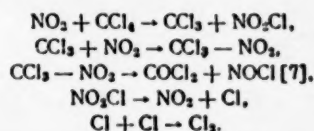
Phosgene, nitrosyl chloride, and chlorine were found to be present in the tube. The reaction which takes place can be expressed by the following equation:



NO_2 , being a radical [10], will apparently react with CCl_4 by a radical mechanism at temperatures above 250°, as expressed by the equations



or

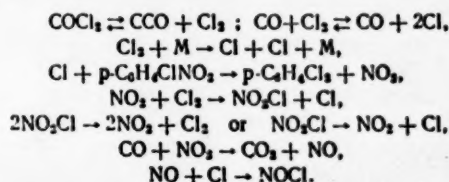


Reaction of COCl_2 with p- $\text{C}_6\text{H}_4\text{ClNO}_2$. Into a tube with a capacity of 9.1 ml, 0.110 g of p- $\text{C}_6\text{H}_4\text{ClNO}_2$ and 0.160 g of COCl_2 were placed.

τ , min	0	41	42	45	48	50	53	55	64	68	80
t , °C	16	215	218	225	234	238	245	250	266	273	290
I , %	0	0	1	3	12	24	40	46	28	18	25

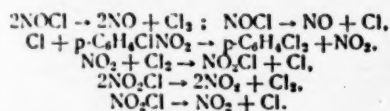
p-Dichlorobenzene could be separated from the reaction products with a yield corresponding to 87% of the theoretical. COCl_2 , CO_2 , and NOCl were found to be present in the gases.

Phosgene may serve as a source of molecular chlorine and under some conditions possibly also of atomic chlorine [11]. Taking into consideration this reaction, which takes place at temperatures above 220°, one may write the following equations:

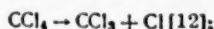


Reaction of NOCl with p-C₆H₄ClNO₂. On heating of p-chloronitrobenzene with an excess of NOCl at 205°, the absorption of light by the tube after its heating for 0, 2, 5, 7, 10, 15, 20, 25, 30, and 35 min was 0, 13, 25, 35, 42, 48, 51, 55, 54, and 55%. A dark-colored liquid having a bluish tinge condensed in the tube after cooling. p-Dichlorobenzene, NO, NO₂, and NOCl were found among the reaction products.

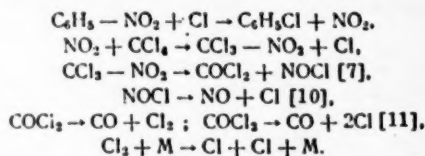
As has been pointed out by N. N. Semenov [10], nitrosyl chloride may decompose with the formation of NO and of atomic chlorine that is capable of initiating a chain process. In this case the interaction between NOCl and p-chloronitrobenzene which takes place above 200° can be expressed by the following equations.



Mechanism of the reaction between CCl₄ and C₆H₅NO₂. Polychloroalkanes, for example CCl₄, react with aliphatic hydrocarbons by a radical mechanism at temperatures as low as 130-140° [11]. Taking into consideration the high temperature at which the reaction of CCl₄ with aromatic nitrocompounds takes place and also the nature of the substances that form as intermediate products, one may assume that the reaction between the substances in question proceeds by a chain mechanism in such a manner that the chain originates as follows

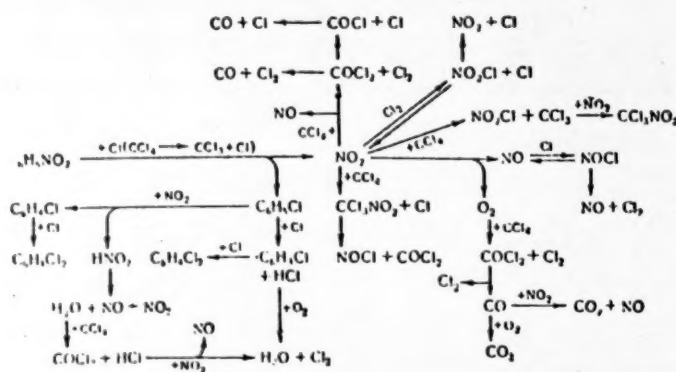


and develops as formulated below:



Termination of the chain may take place by recombination of radicals and atoms or in some other way.

Investigation of the kinetics of the reaction of aromatic nitrocompounds with CCl₄ indicated that this reaction is of a complex nature and that it involves a number of successive and parallel reactions which proceed simultaneously. In the case of nitrobenzene, the process can be represented by the following general scheme:



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MECHANISM OF THE THERMAL BREAKDOWN OF PERCARBONATES IN SOLUTION

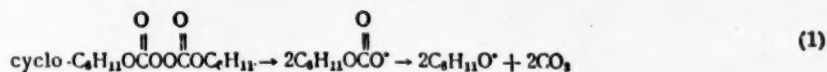
Corresponding Member AN SSSR G. A. Razuvaev,

L. M. Terman, and G. G. Petukhov

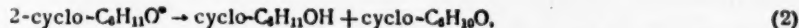
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 3, pp. 628-630,
January, 1961

Original article submitted September 29, 1960

In our paper [1] on the decomposition of dibenzyl and dicyclohexyl percarbonates in various solvents it was found that the RO radicals, which resulted from scission of the molecule



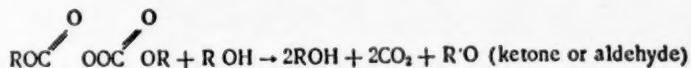
disproportionated in some solvents such as benzene, carbon tetrachloride and acetic acid



and the solvents took no part in the radical reactions. It is very likely that process (2) takes place in a "cage" of solvent. In alcohols we observed that the solvents did take part, giving hydrogen to the RO radicals, and being oxidized to aldehydes or ketones.

In the present work we have investigated the reaction between the RO radicals and the solvent, using a radical trap α, α -diphenyl- β -nitrilhydrazyl (DPPH) and also using labelled atoms. In Figs. 1 and 2 [which are in coordinates $\ln^* (C_0/C)$ vs t , where C_0 is the initial concentration of percarbonate in the solution, and C is its concentration at time t] is shown the rate of decomposition of dicyclohexyl percarbonate in carbon tetrachloride and benzene (0.1 mole/liter) and in isopropanol (0.06 mole/liter). It is evident from Figs. 1 and 2 that the addition of DPPH has no effect at all on the rate of decomposition in carbon tetrachloride and benzene (this is shown by the absence of an initiation period for the decomposition in these solvents), whereas the addition of DPPH completely stops the decomposition process in isopropanol.

For a more detailed study of the mechanism of percarbonate decomposition in alcohols, which proceeds according to the general equation



the system in which $\text{R} = \text{R}'$ was investigated. The most convenient radical was iso-C₃H₇ = $\text{R} = \text{R}'$. We introduced the labelled C¹⁴ into both the isopropyl radical from scission and into the alcohol. The acetone, which was separated from the reaction mixture from the decomposition of C¹⁴-labelled diisopropyl percarbonate in unlabelled isopropanol, was completely nonradioactive.

When the same reaction was carried out with nonradioactive peroxide in C¹⁴-labelled alcohol, the activity of the acetone corresponded to that of the alcohol (Table 1).

* As in original, Cf. figure ordinates.

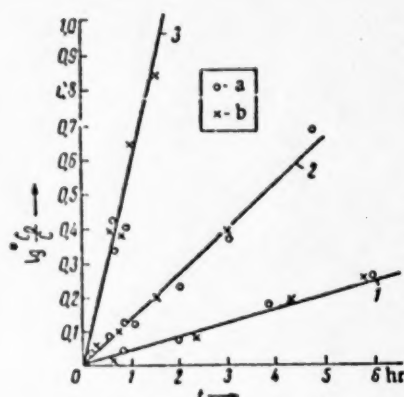


Fig. 1. Decomposition of dicyclohexylpercarbonate $C_0 = 0.1$ mole/liter. 1) in CCl_4 , $t = 50^\circ$; 2) in C_6H_6 , $t = 50^\circ$; 3) in C_6H_6 , $t = 60^\circ$. a) Without DPPH; b) with DPPH.

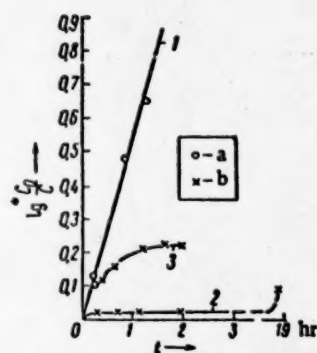


Fig. 2. Decomposition of dicyclohexylpercarbonate in $iso-C_3H_7OH$. $C_0 = 0.06$ mole/liter, $t = 25^\circ$. 1) Without DPPH; 2) with DPPH; 3) DPPH added 15 min after the beginning of the reaction.

TABLE 1

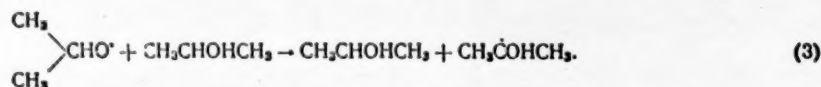
Decomposition of Diisopropyl Percarbonate in Isopropanol. $C_0 = 0.2-0.4$ mole/liter; $t = 50-60^\circ$

Activity, counts/min*		Activity of acetone 2,4-dinitrophenylhydrazone		Activity of Isopropanol separated after the reaction		
diisopropyl percarbonate**	Isopropanol**	counts/min	% of initial activity	counts/min	taking dilution into account	% of initial activity
Inactive	48 300	43 920	91.2	—	—	—
72 000	Inactive	1170	1.6	1890	74 000	102.5

* Radiometric analysis was carried out in an internally filled counter. Error of the measurements $\pm 3\%$.

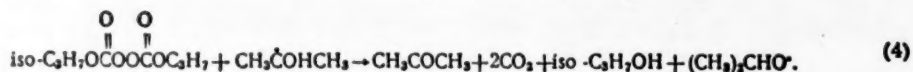
** It was assumed that the peroxide and the alcohol were labelled at the second carbon.

On the basis of the results obtained it can be concluded that the isopropyl radicals arising from the peroxide according to Eq. (1) are finally transformed into the alcohol by abstraction of hydrogen from the solvent



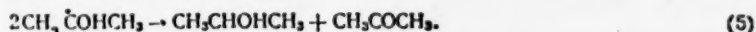
On the basis of Kharasch's work [3] it is known that free radicals abstract hydrogen from the C-H groups of isopropanol and form new alcohol radicals which in our case are isomeric with the radicals formed from the peroxide.

It should be supposed that this radical initiates decomposition of the peroxide:



This explains why acetone is formed only from alcoholic solvents. (In view of the small concentration of peroxide in solution one can ignore the small amount of alcohol which is formed from the peroxide and could then take part in reactions with radicals. At the end of the decomposition its quantity would amount in all to 5 g/liter.)

It may be thought that, in spite of Eq. (4), the acetone could be formed by disproportionation of the alcohol radicals



This equation is generally used to explain the formation of acetone in the radical dehydration of isopropanol [2]. In order to decide whether this reaction really took place we used isopropanol deuterated in the hydroxyl group as the solvent for decomposition of diisopropyl percarbonate. According to Eq. (5), this should give acetone and $\text{CH}_3\text{CDODCH}_3$.

The alcohol, washed free from deuterated hydroxyl, was shown not to contain deuterium by isotopic analysis and by IR spectrum. Our observation is in agreement with a recently published paper [3] in which the optical activity of secondary butanol was used in the photolysis of benzophenone. The absence of disproportionation (5) was shown by retention of optical activity in the alcoholic solvent.

Thus the decomposition reaction of diisopropyl percarbonate in isopropanol can be explained by the successive reactions (1), (3) and (4).

TABLE 2

Initiation of Reaction between CCl_4 and Isopropanol at 60° (in moles of HCl separated per mole of peroxide added)

	Peroxide concentration, mole/liter			
	0.04	0.02	0.01	0.005
Benzoyl peroxide	—	5.27	5.65	13.65
Dibenzyl percarbonate	—	19.7	39.4	66.0
Dicyclohexyl percarbonate	12.0	41.0	64.5	112

On the basis of the data obtained it would be expected that percarbonates would be active initiators for the reaction between carbon tetrachloride and alcohols described earlier [4]. Data on this reaction are given in Table 2.

Using benzoyl peroxide and other acyl peroxides to initiate this process, it remains unclear as to what starts this reaction: the $\text{CCl}_3\dot{\text{C}}$ radicals derived from the peroxide radicals and CCl_4 , or the $\text{CH}_3\dot{\text{C}}\text{OHCH}_3$ radicals formed from peroxide radicals and isopropanol.

In the example using percarbonates it was shown that the initial process is the reaction of the radicals, formed according to Eq. (1), with the alcohol.

Because RO^\bullet radicals, in distinction from R^\bullet radicals, do not react with CCl_4 , the yield of active $\text{CH}_3\dot{\text{C}}\text{OHCH}_3$ radicals per mole of peroxide would be considerably higher when percarbonates are the initiators.

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ELECTROPHILIC SUBSTITUTION AT A SATURATED CARBON ATOM

INFLUENCE OF THE MEDIUM ON THE MECHANISM OF ISOTOPIC EXCHANGE BETWEEN
THE ETHYL ESTER OF α -BROMOMERCURIPHENYLACETIC ACID AND MERCURIC
BROMIDE LABELLED WITH Hg^{203}

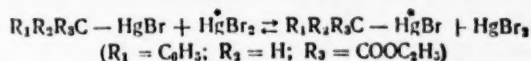
Corresponding Member AN SSSR O. A. Reutov, V. I. Sokolov
and I. P. Beletskaya

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January, 1961

Original article submitted September 16, 1960

It is known that the medium is one of the basic factors which determines the rates and mechanisms of reactions. Change of the medium can lead to a change in the rate of a reaction or to a partial change in the mechanism, which leads to complicated kinetics (mixed kinetic order). A considerably more abrupt change in the properties of the medium causes a complete change in mechanism of the process. A particular case which has been studied in sufficient detail is nucleophilic substitution at a saturated carbon atom. In recent years an intensive investigation has begun of electrophilic substitution reactions. However a systematic study of the effect of the nature of the solvent on the mechanism of electrophilic substitution at a saturated carbon atom has not been carried out until now. Some conclusions can be drawn from a series of papers by Cram [1-9] in which he studied the effect of the solvent on the stereochemical (but not the kinetic) results of heterolytic fission of the carbon-carbon bond.

In the present paper the change of kinetic order and reaction mechanism of electrophilic substitution at a saturated carbon atom on changing the solvent is reported for the first time. The isotopic exchange reaction of the ethyl ester of α -bromomercuriphenylacetic acid with mercuric bromide labelled with Hg^{203} was chosen for investigation:



The kinetics of the reaction were studied in pyridine and 70% aqueous dioxane.* It was shown that in pyridine the reaction was of second order over-all (first order in each component)

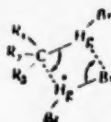
$$K_2 = 6.60 \cdot 10^{-2} \text{ liter/mole} \cdot \text{sec at } 60^\circ.$$

The parameters of the Arrhenius equation: $E = 16.3 \text{ kcal/mole}$, $\log A = 9.5$, Entropy of activation $\Delta S = -15.5$ entropy units at 60° .

$$K_2 = 10^{9.5} \exp\left(-\frac{16300}{RT}\right).$$

* The experiment will be completely published in Izvestiya Akad. Nauk SSSR, Otdel. Khim. Nauk.

We believe that reaction takes place between a molecule of the organomercurial and a molecule of mercuric bromide via a complex



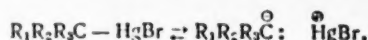
with simultaneous nucleophilic solvation of the leaving mercury atom, which facilitates the process considerably. In fact the pyridine complex of mercuric bromide, $C_5H_5N \cdot HgBr_2$, takes part in the reaction.

On studying isotopic exchange in 70% aqueous dioxane it was found that the reaction is of first order overall: first order in the organomercurial and zero order in mercuric bromide.

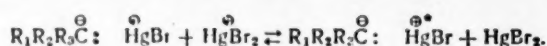
$$K_1 = 5.58 \cdot 10^{-4} \text{ sec}^{-1} \text{ at } 60^\circ.$$

The parameters of the Arrhenius equation are $E = 26.7$ kcal/mole, $\log A = 14.3$. The entropy of activation is $\Delta S = +4.6$ entropy units at 60° .

This is the first time that first order kinetics have been observed in an electrophilic isotopic exchange reaction. This result can be explained by the fact that the slowest step, which determines the over-all rate, is the ionization of the organomercurial compound.* It is likely that this ionization leads to the formation of an ion pair**



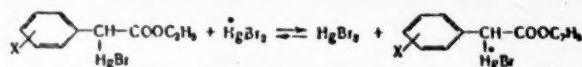
which in the second fast stage exchanges with mercuric bromide



Thus it is plain that a change in solvent led to a change in reaction mechanism. As far as we know no case of kinetic confirmation of the S_E1 mechanism has been published until now.

Comparison of the results obtained by carrying out the reaction in pyridine and in aqueous dioxane showed that the reaction is considerably facilitated; This arises first of all from a sharp decrease in activation energy. We have noted that the addition of pyridine strongly accelerates the exchange reaction in dimethyl formamide. The possibility is not excluded that by varying the medium conditions will be created in which one can observe the gradual change of the kinetics from first order to second order.

We have studied the effect of structural factors on the rate of reaction (for example, of the ethyl esters of different α -bromomercuriarylacetic acids) of isotopic exchange in aqueous dioxane, in which the kinetics are first order



where $X = p-F, p-Cl, p-Br, p-I, p-CH_3, p\text{-tert-}C_4H_9, o-CH_3$. The substituents can be placed in the following order according to their effect on the reaction rate*** (in order of deceleration);

X	p-I, Br, Cl	p-F	H	o-CH ₃	p-CH ₃	p-C ₄ H ₉
Time of half-exchange, min	340	500	620	1500	2000	3000

which agrees with the postulated S_E1 mechanism.

* The considerable lability of the C-Hg bond in compounds similar in structure to those studied is well known [10, 11].

** It is evident that ionization [12, 13], and not dissociation, has occurred in this case because it is unlikely that the given reaction could proceed with kinetically free charged particles.

*** The precision of this method does not permit one to distinguish between the effects of chlorine, bromine and iodine.

It is known that alkyl substituents (independent, to a first approximation, of whether they are o- or p-) donate electrons which ought to increase the electron density at the reactive center and thus impede ionization, but the halogens, which withdraw electrons, partially neutralize the charge of the nascent benzyl carbanion, stabilizing it and thus facilitating ionization.



The question of the stereochemistry in this S_N1 reaction still remains obscure.

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AN INFRARED ABSORPTION SPECTRAL STUDY OF THE STRUCTURE
OF LITHIUM ALKOXIDES
THE O-LI...O BOND

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Structural studies on organolithium compounds by various methods (IR spectra, cryoscopy, dipole moments [1-3]) have shown that these compounds are associated. The complexes of organolithium compounds are, in their nature, similar to the known complexes of B, Be, Al, which arise by the formation of three-centered molecular orbitals which are formed from the primary B-H, Be-C, Al-C, etc. chemical bonds [4, 5]. In distinction from the groups Li-C, Al-C etc., the groups Li-O, Al-O and others can form secondary chemical bonds not only by the formation of many-centered electronic molecular orbitals, but also by acceptor-donor interaction. Consequently complexes in which Li-O, Al-O and other groups take part should be stronger than complexes containing bonds of the first type.

The present work was intended to study the structure of the compounds R-O-Li and to test experimentally the conclusions reached above about their complex formation.

Of the lithium alkoxides made by us lithium tertiary-butoxide, tert-C₄H₉OLi, was studied in most detail. It is very soluble in various organic solvents. This compound was prepared by the action of lithium metal on tertiary butanol in diethyl ether, and it was then separated in a crystalline form and purified by fourfold recrystallization from ether and hexane.

The lithium alkoxides were prepared under argon and all operations with them were carried out under argon.

With the idea of studying the properties of the O-Li bond the specific conductivity of tert-C₄H₉OLi was measured in 1.17 N solution in hexane at room temperature. The specific conductivity was less than $2 \cdot 10^{-7}$ ohm⁻¹. V. N. Vasil'eva measured the dipole moment of lithium tert-butoxide in hexane solution at 25°C and found it to be close to 0.74 D.

Finally V. A. Dubovitskii and O. V. Nogina kindly carried out cryoscopic molecular weight determinations on 0.088 N lithium tert-butoxide solution in cyclohexane at room temperature. The results showed it to have a degree of association equal to five (mol. wt. calculated 80.06, found 396). The value for the dipole moment mentioned above also points to a complex whose formation is possible also in hexane solution.

Thus the data obtained permit conclusions to be drawn about the covalent nature of the Li-O link in lithium tert-butoxide and also about the occurrence of association even in weak solutions. IR spectra of lithium tert-butoxide were measured in the crystalline state and in solutions. These spectra confirm the conclusions mentioned above. The spectra were obtained using Hilger double beam IR spectrometers IKS-14 and N-800.

The IR spectra of lithium tert-butoxide in hexane, CCl₄, cyclohexane, dioxane, diethylamine and triethylamine do not differ much from the spectrum of a crystalline sample. An increase in the temperature of the triethylamine solution to 70-80°C did not lead to a notable change in the spectrum. The indifference of lithium tert-butoxide to active solvents and increased temperature is evidence for the great stability of these complexes.

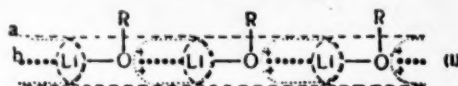
TABLE 1

Crystalline state (paste in vaseline or fluorinated oil)	1.17 N solution in hexane; thickness 50 μ .	0.4 N solution in CCl_4 ; thickness 50 μ	Frequency assignments [6-9]
2945 (v.s.) 2850 (s.) 1925 (w.) 1470 (w.) 1375 (m.) 1353 (s.)	~2950 (s.) ~2850 (m.) ~1460 (w.) 1378 (w.) 1355 (m.)	2950 (s.) 2850 (m.) 1467 (m.) 1378 (m.) 1354 (s.)	C-H bond vibration Deform. vib. of CH_3 group
1209 (v.s.) 1013 (m.) 970 (v.s.)	1212 (v.s.) 1012 (w.) 971 (s.)	1210 (v.s.) 1009 (w.) 971 (s.)	C-O bond vibration Deform. vib. (rocking) of CH_3 group C-O-(Li)
882 (w.)	868 (v.w.)	880 (v.w.)	Deform. vib. (rocking) of CH_2 group
748 (m.) 578 (v.s.) 507 (s.) 462 (m.) ~395 (s.)	746 (m.) 580 (s.) 510 (m.) 463 (m.) ~400 (m.)	? 579 (s.) 510 (m.) 461 (m.) 400 (m.)	C-C bond vibration Association vib. O-Li C-C-C deform. vib.

A rough calculation carried out for lithium methoxide showed that it would be expected that the bond vibration frequency for the free Li-O group would appear in the region $1400-1700\text{ cm}^{-1}$; however data from papers on the IR spectra of alcohols [6-9] and the spectra of tert- C_4H_9ONa and tert- C_4H_9OK (which we made for comparison) do not permit the assignment of a band in the region indicated, or in any other region, to the vibration of the free group O-Li. However intense bands in the long wavelength region of the spectrum with frequencies of 580 and 510 cm^{-1} should be assigned to complex vibrations of a chain containing lithium bonds (bridges).... Li-O...Li-O...Li-, in the complex which possibly has a steric structure in the pentamer. These bands are absent from the spectrum of tert-butanol and disappear on decomposition of lithium tert-butoxide in air.

Funk [10], who studied the combination dispersion and IR spectra of beryllium and lithium acetylacetonates, assigned a band with frequency 510 cm^{-1} to the vibration of the metal-ligand bond in the latter case. The nature of the bond in the O-Li...O bridge of the pseudo-aromatic ring of lithium acetylacetonate [11] differs little from that discussed in our example, but it is evident that the former is the more stable.

The considerable stability of lithium tert-butoxide complexes can be explained in two ways: 1) the formation of three-center intermolecular electronic orbitals by allotting the free p-orbital of the lithium atom of one molecule to the electrons taking part in the σ -bond O-Li of another molecule; in this way one pair of valence electrons take part in the formation of two bonds O-Li...O (Ia); 2) acceptor-donor interaction by using an unshared pair of p-electrons on an oxygen atom and the free p-orbit of the lithium in another molecule, which increases the stability of the intermolecular bond (Ib). In the case under discussion one can evidently speak of considerable delocalization of electrons with the formation of many centered molecular orbitals, if one bears in mind the overlap of three-center molecular orbitals and the part played in the formation of the intermolecular bond by the unshared p-electron pair from oxygen. One can postulate in the crystals a peculiar polymer chain containing a number of pseudo-conjugated O-Li...O bonds as in (I)



or any other formulation with effective delocalization of the electrons which could lead to a decrease in the energy difference between the ground and excited states of the system. The basis for such a suggestion is the observation of luminescence in compounds of this type.

We obtained luminescence spectra of lithium tert-butoxide in the crystalline state and in hexane solution (sufficiently bright in the crystalline case but considerably less strong in solution) with an exciting wavelength of 365 m μ at $T = 77^\circ\text{K}$. The luminescence spectrum appeared as a broad band with a maximum in the region of 430 m μ . In hexane solution the maximum of the fluorescence band was about 410 m μ . The absorption of light by systems within our terms of reference can be explained by transition of an electron from a ground state multicenter molecular orbital. Another possibility for the excitation of the system is transition of an electron from an unshared pair on an oxygen atom into an excited multicenter orbital.

Apart from the compounds described the IR spectra of a series of lithium alkoxides with normal aliphatic chains were also studied: CH_3OLI , $\text{C}_2\text{H}_5\text{OLI}$, $n\text{-C}_3\text{H}_7\text{OLI}$, $n\text{-C}_4\text{H}_9\text{OLI}$. These alkoxides were crystalline substances which decomposed in air and which dissolved slightly or not at all in organic solvents (hexane, cyclohexane, benzene, toluene, pyridine, dioxane, diethylamine, triethylamine, etc.). This prevented us from obtaining sufficiently clear-cut spectra in solution. The spectra of crystalline samples (pastes in vaseline or fluorinated oils) are cited in Table 2 (frequency in cm^{-1}).

Bearing in mind that lithium tert-butoxide is strongly associated, it may be considered that the lithium alkoxides with unbranched aliphatic radicals are even more strongly associated, which explains their insolubility or poor solubility (alkoxides with longer carbon chains) in those solvents in which lithium tert-butoxide dissolves easily. The considerable association in the compounds R-O-Li is in agreement with the ability of metal alkoxides to polymerize [20]. The compounds $n\text{-R-O-Li}$ also give luminescence spectra (we shall not discuss this in detail in the present paper), which possibly confirms the presence of molecular association in the crystalline state. From this point of view, and taking into account data on the IR spectra of the corresponding alcohols, the germanium and aluminum alkoxides, etc. [6, 12, 13-19], the spectra of sodium and potassium methoxides and ethoxides which we prepared for comparison, and also the change in bonds in the spectra when R-O-Li reacts with air (erosion of the bands until they disappear) one can make approximate assignments of the bands in the spectra, and in particular one can assign to the complex association vibration of the group O-Li the complex bands with frequencies CH_3OLI 670 cm^{-1} , 537 cm^{-1} ; $\text{C}_2\text{H}_5\text{OLI}$ 675 cm^{-1} , 515 cm^{-1} , 457 cm^{-1} (?); $n\text{-C}_3\text{H}_7\text{OLI}$ 576 cm^{-1} , 527 cm^{-1} , 498 cm^{-1} ; $n\text{-C}_4\text{H}_9\text{OLI}$ 565 cm^{-1} , 483 cm^{-1} .

TABLE 2

Crystalline CH_3OLI	Assignment of basic frequencies	Crystalline CH_3OLI	Assignment of basic frequencies
2923 (m)	Bond vibration C-H	1060 (v.s.)	Bond vibration C-O
2842 (s)		862 (w)	?
2792 (s)		760 (w)	
2595 (w)	?	670 (m)	Association vibration
2080 (w)	2-val C-O	585 (m.sh.)	
1570 (m)	?	537 (s)	
1435 (s)	CH ₃ deformation	428 (s)	Deformation of CH ₃
1368 (s)		410 (m.sh.)	relative to C-O
1160 (m)	-OCH ₃		

$\text{C}_2\text{H}_5\text{OLI}$: 2957 (s), 2917 (m.sh.), 2848 (s), 2808 (s), 2713 (m), 2606 (m), 2123 (w), 1794 (w), ~1490 (m.sh.), ~1455 (s. unresolved), 1435 (s), 1378 (v.s.), 1363 (m.sh.), 1155 (s), 1107 (v.s.), 1058 (v.s.), 970 (m., sh.), 885 (s), 720 (m), 675 (s), 515 (s), 457 (m.sh.), 428 (m), 405 (m).

$n\text{-C}_3\text{H}_7\text{OLI}$: 2945 (s), 2910 (m), 2860 (m), 2835 (m), 2790 (s), 2700 (m), 2660 (w), 2600 (v.w.), 2155 (w), ~1630 (m. broad), 1450 (m), 1380 (s), 1297 (w), 1247 (w), 1153 (m.sh.), 1110 (s), 1078 (v.s.), 1015 (m), 976 (w), 882 (s), 576 (s), 527 (s), 498 (m), 450 (m), ~395 (s).

$n\text{-C}_4\text{H}_9\text{OLI}$: 2950 (v.s.), 2905 (v.s.), 2843 (s), 2800 (s), 2710 (m), 2595 (w), 1625 (m), ~1455 (s), 1432 (s), 1375 (s), 1155 (m), 1120 (m), 1085 (v.s.), 1002 (m), 970 (w), 905 (w), 882 (w), 800 (w), 730 (m) ?, 672 (w), 565 (v.s.), 483 (s), 435 (v.s.), ~400 (s).

However a more exact assignment of the spectral bands and more definite conclusions about the lithium alkoxides with normal aliphatic radicals will become possible as the result of data from isotopic substitution

(D, Li⁶) studies, x-ray structural analysis [21] and calculations of the vibrations of the initial free and associated R-O-Li molecules.

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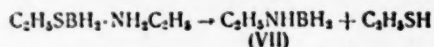
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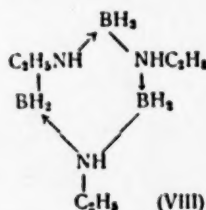
SYNTHESIS AND SOME PROPERTIES OF TRIS-(ETHYLMERCAPTO)-DIBORANE

Original article submitted July 4, 1960

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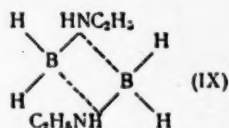


The trimer of ethylamino-borane (VIII)



is a solid substance, completely stable in air, which does not react with water or alcohols at room temperature. Hydrolysis was successfully accomplished only by boiling with 20% hydrochloric acid. This compound has analogous chemical properties to the trimer of methylamino-borane [2].

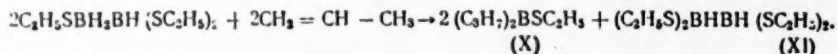
Ethylamino-borane occurs in the form of a dimer as well as a trimer. On distilling the products of reaction one obtains, along with N-triethylborazole, a liquid with b. p. 85-90°/2 mm which analyzes correctly for ethylamino-borane and whose molecular weight is intermediate between that for the dimer and the trimer. Evidently this fraction is a mixture of the dimer (IX) and trimer (VIII) of ethylamino-borane. The dimer changes into the trimer on standing.



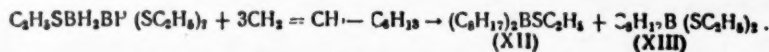
The dimer (IX) differs from the trimer (VIII) in its chemical properties. It is considerably less stable to oxygen and moist air. Both forms are transformed into N-triethylborazole on heating, but at different rates. Whereas the trimer only begins to lose hydrogen at 140-150° and needs to be heated to 180° for complete conversion, the dimer is partially converted to N-triethylborazole on distillation in vacuum. On heating a mixture of approximately 35% of the dimer and 65% of the trimer, hydrogen evolution begins at 100°. In the 100-120° range evolution of hydrogen ceased when about one third of the theoretical of hydrogen had separated, and it only recommenced when the temperature was raised to 150°.

We further studied the behavior of tris-(ethylmercapto)-diborane in relation to unsaturated compounds. It has been shown earlier [1] that bis-(n-butylmercapto)-diborane reacts with olefinic hydrocarbons in ethereal solution at room temperature to form the n-butyl esters of dialkylthioboric acids, whereas tetrakis-(n-butylmercapto)-diborane adds across a double bond in more vigorous conditions.

Tris-(ethylmercapto)-diborane behaves analogously toward propene, with which it gives an addition reaction whose product is only the more highly hydrogenated half molecule, the ethyl ester of di-n-propylthioboric acid (X). The second unreacted half-molecule of tris-(ethylmercapto)-diborane dimerizes to tetrakis-(ethylmercapto)-diborane (XI).



Tris-(ethylmercapto)-diborane does not react with ethylene or octene at room temperature. In boiling ethereal solution tris-(ethylmercapto)-diborane and octene form a mixture of the esters of di-n-octylthioboric acid (XII) and n-octylthioboric acids (XIII). However in this case the addition reaction is accompanied by symmetrization, which leads to the formation of triethylthioborate and tri-n-octylboron in addition to the esters mentioned.



EXPERIMENTAL

Tris-(ethylmercapto)-diborane. Diborane (0.16 mole) was passed for 5 hr at room temperature into a solution of 37.2 g (0.6 mole) of ethylmercaptan in 100 ml absolute ether. The whole was mixed in a three-necked flask with a stirrer, a gas inlet tube, and a reflux condenser. Hydrogen was evolved and the mixture became viscous.

On the following day ether and residual ethylmercaptan were removed in vacuum, and the residue (33.0 g) was distilled. There was obtained 21.0 g of tris-(ethylmercapto)-diborane (63.5%), b. p. 105-110°/2 mm; d_4^{20} 0.9887; n_D^{20} 1.5360.

Found %: C 33.57, 33.60; H 9.25, 9.23; B 10.4, 10.8. $C_6H_{18}B_2S_3$. Calculated %: C 34.63; H 8.72; B 10.44.

Mol. wt.* found 202.0, calculated 208.06.

However on distilling 4.3 g of a liquid condensed into a trap at -70°. This liquid was not quite pure bis-(ethylmercapto)-diborane.

Triethylthioborate. 27.0 g (0.43 mole) of ethylmercaptan was added over 3.5 hr to (I) (19.0 g, 0.09 mole) at 140°. Hydrogen (6850 ml) was evolved. The reaction products were distilled to yield 24.1 g triethylthioborate, b. p. 93-96°/2 mm, d_4^{20} 1.0191, n_D^{20} 1.5465; M_R^{20} * found 60.39, calculated 59.97.

Found %: C 37.59, 37.37; H 7.61, 7.79; B 5.88, 5.85. $C_6H_{15}BS_3$. Calculated %: C 37.11; H 7.79; B 5.57.

The yield of triethylthioborate was 69% of theoretical.

Effect of ethylamine on tris-(ethylmercapto)-diborane. Ethylamine (17.0 g, 0.38 mole) was added to tris-(ethylmercapto)-diborane (39.0 g, 0.188 mole) in a two-necked flask with a dropping funnel and a reflux condenser connected to a gas pipette. The reaction mixture became warm but no hydrogen was evolved. Ethylmercaptan (26.4 g; 75%) was evaporated off at the water pump, beginning at room temperature and continuing by heating the reaction mass on a water bath (bath temperature 30-40°).

The residue was fractionally distilled to give 10.1 g N-triethylborazole (50% of theory), b. p. 68-70°/23 mm, n_D^{20} 1.4380 (lit. data; b. p. 66-68°/20 mm, n_D^{20} 1.4370 [1]); and 4.6 g of ethylamino-borane trimer (21% of theory), m. p. 171-173° (recrystallized from benzene).

Found %: C 42.18, 42.38; H 13.95, 13.89; B 19.29, 19.31; H_{act} 3.48, 3.61. $(C_2H_7NB)_3$. Calculated %: C 42.21; H 14.16; B 19.01; H_{act} 3.55.

Mol. wt. found 181.4, calculated 170.73.

A liquid (3.3 g, b. p. 85-90°/2 mm; n_D^{20} 1.4593) was also separated, which appeared to be a mixture of the dimer and trimer of ethylamino-borane.

Found %: B 17.59, 17.94; H_{act} 3.39, 3.82. C_2H_7BN . Calculated %: B 19.01; H_{act} 3.55.

A determination of the molecular weight gave values of 153.3, 147.6, which corresponds to a mixture of 35% dimer and 65% trimer.

3.2 g of the mixture was heated under reflux. Gas evolution began at 100° and 450 ml of hydrogen separated in the range 100-120° (35% of theory), but then gas evolution ceased; only when the temperature was increased to 150° did hydrogen evolution recommence. The mixture was heated to 180-200° to complete the reaction. In all 1100 ml of gas (87% of theory) was evolved. The residual liquid was distilled and gave 1.7 g N-triethylborazole (53%), b. p. 68-70°/23 mm, n_D^{20} 1.4365.

* The molecular weight was determined cryoscopically in benzene.

** The molecular refractivity was calculated as the sum of bond refractivities. For the values of the bond refractivities of C-C, C-H, C-S, C-N, N-H see [3] and for B-C [4]. The bond refractivity for B-S was taken equal to 5.70 by comparing the molar refractivities of boron-sulfur compounds, and in a similar way the bond refractivity for B-H was calculated to be 1.57.

Effect of propene on tris-(ethylmercapto)-diborane. Propene was passed into a solution of tris-(ethylmercapto)-diborane (44.7 g, 0.22 mole) in 200 ml absolute ether until spontaneous heating of the reaction mixture ceased. After removing the solvent, the residue was fractionally distilled in vacuum, 17.4 g (25% of theory) of ethyl di-n-propylthioborate was obtained with b. p. 40-50°/1 mm. After a second distillation the ester had b. p. 61-65°/8 mm, d_4^{20} 0.8214, n_D^{20} 1.4576; MR_D found 52.49, calculated 52.13.

Found %: C 62.03, 61.96; H 12.41, 12.35, C₈H₁₃BS. Calculated %: C 60.76; H 12.11.

19.4 g (33% of theory) of tetrakis-(ethylmercapto)-diborane, b. p. 75-85°/1 mm, d_4^{40} 0.9755, n_D^{20} 1.5206; MR found 83.66, calculated 83.14.

Found %: B 7.84, 7.50, C₈H₂₂B₂S₄. Calculated %: B 8.07.

4.1 g (10% of reacted material) of the initial tris-(ethylmercapto)-diborane, b. p. 102-110°/1 mm.

Effect of octene on tris-(ethylmercapto)-diborane. A mixture of tris-(ethylmercapto)-diborane (17.4 g, 0.08 mole), octene (33.6 g, 0.3 mole) and 25 ml absolute ether was boiled for 50 hr (temperature of the reaction mixture 55-60°). After removal of ether and excess octene the residue was fractionally distilled in vacuum. The products obtained were: 1) 3.2 g (10% of theory) triethylthioborate, b. p. 51-58°/0.1 mm, n_D^{20} 1.5376; 2) 1.8 g (10% of reacted material) of the initial tris-(ethylmercapto)-diborane, b. p. 68-75°/0.07 mm, n_D^{20} 1.5322; 3) 7.8 g (20% of theory) diethyl n-octylthioborate, b. p. 85-98°/0.05 mm, d_4^{20} 0.8888, n_D^{20} 1.4804; MR_D found 78.78, calculated 79.29.

Found %: B 4.03, 4.05, C₁₂H₂₇BS₂. Calculated %: B 4.39.

4) 7.2 g (15% of theory) ethyl di-n-octylthioborate, b. p. 116-125°/0.08 mm, d_4^{20} 0.8435, n_D^{20} 1.4663; MR_D found 98.00, calculated 98.66.

Found %: B 3.27, 3.26, C₁₈H₃₉BS. Calculated %: B 3.63.

5) 13.9 g (25% of theory) tri-n-octylboron, b. p. 140-150°/0.06 mm; n_D^{20} 1.4459.

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**ACTION OF TRIETHYLSILANE ON ACETYLENIC γ -GLYCOLS
IN THE PRESENCE OF Pt/C AND H_2PtCl_6**

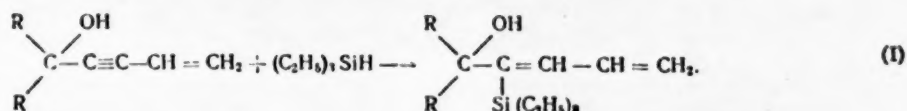
**I. M. Gvardtsiteli, K. I. Cherkezishvili, and Corresponding
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I. V. Stalin Tiflis State University

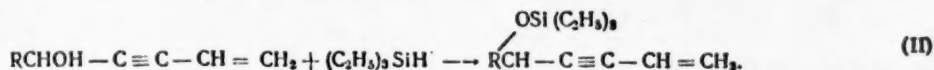
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 4, pp. 817-820,
February, 1961

Original article submitted September 2, 1960

In previous communications [1, 2] we examined the reaction of triethylsilane with secondary and tertiary vinyl ethynylcarbinols in the presence of Pt/C and 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropanol. It was found that in the presence of Pt/C, both secondary and tertiary vinyl ethynylcarbinols give products from addition at the triple bond according to the scheme:



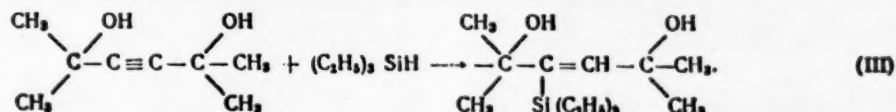
Extremely interesting results were obtained with the use of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropanol [2]. It was found that when this catalyst was used, tertiary vinyl ethynylcarbinols added triethylsilane according to scheme (I), while secondary vinyl ethynylcarbinols added the silane according to scheme (II), i.e., silicoorganic ethers were obtained instead of products from addition at the triple bond:



However, the amount of catalyst was of importance as well as the nature of the alcohol; in the case of n-propylvinylethynylcarbinol, with 2 ml of catalyst the reaction proceeded by scheme (II) and with 1 ml of catalyst, both by scheme (I) and scheme (II) simultaneously.

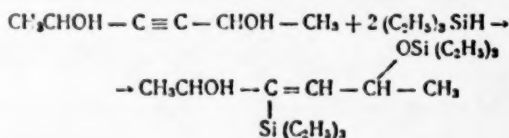
In continuing the work we decided to study the reaction of triethylsilane with acetylenic γ -glycols in the presence of Pt/C and H_2PtCl_6 . We used primary (butynediol), secondary (dimethylbutynediol), and tertiary (tetramethylbutynediol and symmetrical dimethyldiethylbutynediol) glycols.

In the case of Pt/C, tetramethylbutynediol added triethylsilane to give an ethylenic glycol according to the scheme:

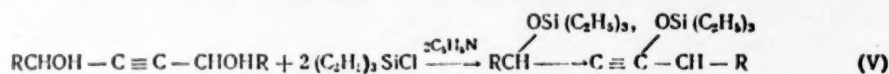
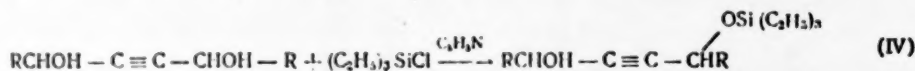


Symmetrical dimethyldiethylbutynediol did not react with triethylsilane under these conditions. According to analysis data, one fraction from the reaction products of butynediol and triethylsilane corresponded to the vinyl ether of triethylsilanol, $(C_2H_5)_3SiOCH=CH_2$.

The reactions studied were repeated with 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropanol. It was found that in the case of tetramethylbutynediol the reaction proceeded by the same scheme more readily and to give higher yields than with Pt/C. While symmetrical dimethyldiethylbutynediol did not react with triethylsilane in the presence of Pt/C, with H_2PtCl_6 the reaction proceeded according to scheme (III) with a yield of 36% of theoretical. The primary glycol, butynediol, reacted according to scheme (III), while the secondary glycol formed a product from simultaneous addition at the triple bond and the hydroxyl:



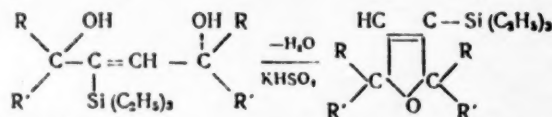
To compare the products of the reaction of primary and secondary glycols with triethylsilane, we decided to prepare mono- and diethers of these glycols from triethylchlorosilane according to the following schemes:



$R = H$ and CH_3 .

The two reactions were carried out under identical conditions with only the ratios of the reagents varied, but it was found that in both cases only the diether was obtained according to scheme (V). The ethers obtained did not correspond to any of the reaction products of the corresponding glycols and triethylsilane.

The organosilicon ethylenic glycols were dehydrated by $KHSO_4$ analogously to ethylenic glycols to form furan compounds according to the scheme:



$R = H$ and CH_3 ; $R' = H, CH_3$ and C_2H_5 .

EXPERIMENTAL

Action of triethylsilane on tetramethylbutynediol in the presence of H_2PtCl_6 . Into a three-necked flask with a mechanical stirrer and reflux condenser were placed 18 g of tetramethylbutynediol, 17 g of triethylsilane, and 1.2 ml of 0.1 M $H_2PtCl_6 \cdot 6H_2O$ in isopropanol. The reaction mixture was heated on a boiling water bath. It crystallized on cooling and was recrystallized from benzene to yield white, lustrous needlelike crystals with m. p. 84.5-86.5° (26.5 g, 75.5% of theoretical) (after recrystallization).

Found %: OH 12.88, 13.41; C 64.82; H 12.00; Si 10.77. $C_{14}H_{30}SiO_2$. Calculated %: OH 13.26; C 64.72; H 11.62; Si 10.84.

Action of triethylsilane on tetramethylbutynediol in the presence of Pt/C. Into a three-necked flask with a mechanical stirrer and reflux condenser were placed 18 g of glycol, 17 g of triethylsilane, and 0.15 g of Pt/C. The reaction mixture was heated on a boiling water bath at 97-98° for 20 hr; the mass crystallized on cooling to room temperature and was recrystallized from benzene to yield white, lustrous crystals with m. p. 84.5-85.5° (18.5 g, 52.89% of theoretical).

Dehydration of 1,1,4,4-tetramethyl-2-triethylsilylbut-2-ene-1,4-diol. A mixture of 7 g of glycol, 1 g of KHSO_4 , and 0.1 g of dithizone was placed in a vacuum distillation apparatus. The mixture was heated in vacuum under nitrogen for 30 min at no higher than 100° and then distilled. We obtained a fraction with b. p. $74-77^\circ$ at 2 mm (5 g); n_D^{20} 1.4590, d_4^{20} 0.8666; MR_D 75.71, calculated 75.75 (76.9% of theoretical yield); hydroxyl not detected.

Found %: C 70.60, 70.47; H 12.10, 12.20; Si 11.30, 11.20. $\text{C}_{14}\text{H}_{28}\text{OSi}$. Calculated %: C 70.00; H 11.66; Si 11.66.

According to analysis data, the substance obtained corresponded to 2,2,5,5-tetramethyl-3-triethylsilyldihydrofuran.

Action of triethylsilane on symmetrical dimethyldiethylbutynediol in the presence of H_2PtCl_6 . The reaction was carried out as above with 10 g of dimethyldiethylbutynediol, 8 g of triethylsilane, and 2 ml of 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol. Distillation yielded the following fractions: (I) 43° (7 mm) 1.4 g; (II) $85-92^\circ$ (2 mm), 2.2 g; (III) $92-100^\circ$ (2 mm) (crystallized); (IV) $145-147^\circ$ (2 mm), 6.5 g.

For fraction IV found: n_D^{20} 1.4870; d_4^{20} 0.9372; MR_D 87.74; calculated MR_D 88.47; found %: OH 10.11, 11.60; calculated %: OH 11.52 (35% of theoretical yield).

Found %: C 67.67, 67.65; H 12.38, 12.12; Si 9.26, 9.55. $\text{C}_{16}\text{H}_{34}\text{O}_2\text{Si}$. Calculated %: C 67.13; H 11.88; Si 9.75.

The substance obtained was symmetrical 1,1,4,4-dimethyldiethyl-2-triethylsilylbut-2-ene-1,4-diol; it formed a very thick colorless liquid.

Dehydration of 1,1,4,4-dimethyldiethyl-2-triethylsilylbut-2-ene-1,4-diol. We used 3.88 g of the substance, 2 g of KHSO_4 , and 0.1 g of dithizone. The mixture was boiled for 20 min and then distilled to yield a fraction with b. p. $88-90^\circ$ (2 mm) (2 g, 55% of theoretical), n_D^{20} 1.4670, d_4^{20} 0.8833, MR_D 84.15; calculated MR_D 85.01; hydroxyl was not detected.

Found %: C 71.35, 71.68; H 12.14, 12.22; Si 9.75, 10.14. $\text{C}_{16}\text{H}_{32}\text{OSi}$. Calculated %: C 71.64; H 11.94; Si 10.44.

The substance synthesized was 2,5-dimethyl-2,5-diethyl-3-triethylsilyldihydrofuran; it formed a mobile, colorless liquid.

Action of triethylsilane on butynediol in the presence of Pt/C . We used 21 g of butynediol, 29 g of triethylsilane, and 0.2 g of Pt/C . After being heated for 20 hr on a boiling water bath, part of the reaction mixture crystallized, and it was then filtered and the filtrate (30 g) distilled. Unreacted triethylsilane (14 g) distilled first and distillation of the residue yielded fractions: (I) $96-97^\circ$ (10 mm), 5.5 g; (II) $97.5-146^\circ$ (3 mm), 0.9 g; (III) 131° (2 mm), 1.3 g; (IV) 139° (2 mm), 1.5 g.

Fraction I had n_D^{20} 1.4414, d_4^{20} 0.8578; found MR_D 48.68; calculated 49.09 (16% of theoretical yield); hydroxyl was not detected.

Found %: C 60.71; H 11.22; Si 18.12. $\text{C}_8\text{H}_{18}\text{OSi}$. Calculated %: C 60.77; H 11.39; Si 17.72.

According to analysis data, the substance corresponded to the vinyl ether of triethylsilanol.

Action of triethylsilane on butynediol in the presence of H_2PtCl_6 . The reaction was carried out under analogous conditions with 21 g of the glycol, 29 g of triethylsilane, and 2 ml of 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol. Distillation yielded the following fractions: (I) 44° (5 mm), 7.6 g; (II) 65° (2 mm), 1.8 g; (III) $104-125^\circ$ (2.5 mm), 5 g, crystals (butynediol); (IV) $127-129^\circ$ (2 mm), 5 g; (V) $139-146^\circ$ (3 mm), 11.7 g; (VI) 150° (2 mm), 7.8 g.

Fraction V was redistilled. We obtained Va with b. p. $60-70^\circ$ (2 mm) and Vb with b. p. $127-129^\circ$ (2 mm), 4 g; the remainder was not distilled. Fractions IV and Vc had the same constants: n_D^{20} 1.4880, d_4^{20} 0.9656; found MR_D 60.27; calculated 60.69; found %: OH 13.26; 15.55; calculated %: OH 16.92; 18% of theoretical yield.

Found %: C 60.20, 60.01; H 11.30, 11.11; Si 13.35, 13.65. $\text{C}_{10}\text{H}_{22}\text{O}_2\text{Si}$. Calculated %: C 59.40; H 10.88; Si 13.86.

The substance we obtained, 2-triethylsilylbutenediol, was a colorless slightly thick liquid.

Dehydration of 2-triethylsilylbutenediol. A mixture of 2 g of the substance, 2 g of KHSO_4 , and 0.1 g of dithizone was boiled for 20 min and then distilled to yield a fraction with b. p. 70-71° (4 mm) (1.2 g, 66% of theoretical yield). Found n_D^{20} 1.4652, d_4^{20} 0.9031; MR_D 56.34; calculated MR_D 57.23; hydroxyl was not detected.

Found %: C 65.40, 64.32, 64.75; H 11.59, 11.47, 11.36; Si 14.94, 15.21, 14.95. $\text{C}_{10}\text{H}_{20}\text{SiO}$. Calculated %: C 65.22; H 10.87; Si 15.22.

According to analysis data, the substance corresponded to 3-triethylsilyldihydrofuran.

Preparation of $(\text{C}_2\text{H}_5)_3\text{SiOCH}_2 - \text{C} \equiv \text{C} - \text{CH}_2\text{OSi}(\text{C}_2\text{H}_5)_3$ from triethylchlorosilane. Into a three-necked flask with mechanical stirrer, reflux condenser, and dropping funnel were placed 5 g of butynediol and 4.4 g of pyridine, and 8 g of triethylchlorosilane added dropwise; the mixture evolved heat strongly and a white precipitate was formed. When all the triethylchlorosilane had been added, the mixture was heated on a boiling water bath for 1.5 hr, the precipitate removed by filtration, and the product vacuum distilled under nitrogen. We obtained fractions I-III. Fraction III had n_D^{20} 1.4558, d_4^{20} 0.9049; found MR_D 94.25; calculated 95.38; 46% of theoretical yield. Hydroxyl was not detected.

Found %: C 60.86, 60.69; H 11.60, 11.39; Si 18.01, 17.20. $\text{C}_{15}\text{H}_{34}\text{O}_2\text{Si}_2$. Calculated %: C 61.14; H 10.83; Si 17.84.

The substance synthesized, 1,4-diethylsiloxybut-2-yne, was a colorless, mobile liquid.

Action of triethylsilane on dimethylbutynediol in the presence of H_2PtCl_6 . The reaction was carried out under analogous conditions with 17.6 g of dimethylbutynediol, 18 g of triethylsilane, and 2 ml of 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropanol. Distillation yielded fractions I-VIII.

Fraction VII had n_D^{20} 1.4740, d_4^{20} 0.9160; MR_D 105.50; calculated MR_D 106.57; found %: OH 5.76; calculated %: OH 5.05; 10% of theoretical yield.

Found %: C 62.31, 62.78; H 11.99, 11.94; Si 15.81, 16.02. $\text{C}_{18}\text{H}_{40}\text{O}_2\text{Si}_2$. Calculated %: C 62.79; H 11.63; Si 16.32.

The substance we synthesized, 3-triethylsilyl-5-triethylsiloxyhex-3-en-2-ol, was a colorless, mobile liquid.

Preparation of $(\text{C}_2\text{H}_5)_3\text{SiOCH} - \text{C} \equiv \text{C} - \text{CHOSi}(\text{C}_2\text{H}_5)_3$ from triethylchlorosilane. We used 8 g of dimethyl-



butynediol, 5.4 g of pyridine, and 10 g of triethylchlorosilane. Distillation yielded fractions I-III. Fraction III had found n_D^{20} 1.4497, d_4^{20} 0.8865; MR_D 103.63; calculated 104.64; 16.8% of theoretical yield. Hydroxyl was not detected.

Found %: C 63.18, 63.15; H 11.42, 11.84; Si 16.09, 16.15. $\text{C}_{18}\text{H}_{38}\text{O}_2\text{Si}_2$. Calculated %: C 63.16; H 11.11; Si 16.37.

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ACID PROPERTIES OF CIS- AND TRANS-ISOMERS OF $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]\text{Cl}_2$ *

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In 1931 [1] one of us measured the acid properties of the trans-isomer of $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]\text{Cl}_2$ and thus provided confirmation for N. Bjerrum's theory of amino acids.

We undertook a quantitative characterization of the acid properties of both stereoisomers of $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]\text{Cl}_2$. The cis- and trans-isomers of $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]\text{Cl}_2$ were prepared by the methods recommended by A. A. Grinberg and B. V. Pritsyn [2]. The cis-isomer was subjected to additional recrystallization. The preparations used were analyzed for Pt and Cl:

trans- $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]\text{Cl}_2$. Found %: Pt 43.17; Cl 15.72. cis- $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]\text{Cl}_2$. Found %: Pt 43.54; Cl 16.14. Calculated %: Pt 43.35; Cl 15.74.

The acid dissociation constants of the isomers were determined by potentiometric titration of their solutions with alkali with the use of a glass electrode by the procedure described previously [3]. The figure gives curves of the titration of 75 ml of 0.005 M solutions of the trans- and cis-isomers with 0.195 N NaOH solution in 0.5 M NaNO_3 solution for providing a constant ionic strength. The figure shows two equivalents of alkali were consumed in the titration of the complex, i.e., the ion $[\text{Pt}(\text{glh})_2(\text{NH}_3)_2]^{2+}$ is a dibasic acid, and as the titration curve showed no breaks, the successive dissociation constants are close to each other.

The dissociation constants were calculated from the titration curves by means of the formula

$$\frac{a_{\text{H}}^2 B}{2a - B} = a_{\text{H}} \cdot \frac{(a - B)}{2a - B} \cdot k_1 + k_1 k_2,$$

which was used by Speakman [4] and others for determining dissociation constants of dibasic acids. In this formula a is the acid concentration in mole/liter, a_{H} is the activity of hydrogen ions, $B = b + a_{\text{H}}$, where b is the concentration of the added alkali in mole/liter, and k_1 and k_2 are the successive dissociation constants. We calculated the constants in the range of 25-75% neutralization of the acid where this formula is most accurate. The dissociation constants determined in this way are not thermodynamic values, as we were unable to allow for the activity coefficients of the complex ions and molecules, and they refer to the given ionic strength. Data from one experiment are given in the table.

The table gives the volume of added NaOH in ml, and X and Y are as follows:

$$X = \frac{a_{\text{H}}^2 B}{2a - B}, \quad Y = \frac{a_{\text{H}}(a - B)}{2a - B}.$$

* glh represents a glycine molecule.

Results of Titrating 0.005 M Solution of trans-[Pt(glh)₂(NH₃)₂]Cl₂ in 0.5 M NaNO₃ with 0.195 N NaOH Solution

V _{NaOH} , ml	pH	$\alpha_{II} \cdot 10^3$	$\alpha_{III} \cdot 10^3$	$\alpha_{IV} \cdot 10^3$	$B = (\alpha + \alpha_{II}) \cdot 10^3$	$(\alpha - B) \cdot 10^3$	$(\alpha - B) \cdot 10^3$	$X \cdot 10^3$	$Y \cdot 10^3$
1.20	2.80	1.58	2.50	3.12	4.70	0.30	5.30	2.20	0.89
1.60	2.94	1.12	1.25	4.16	5.28	-0.28	4.72	1.40	-0.66
2.00	3.04	0.91	0.83	5.22	6.13	-1.13	3.87	1.31	-2.67
2.20	3.14	0.72	0.52	5.73	6.45	-1.45	3.55	0.94	-2.94
2.40	3.22	0.60	0.36	6.27	6.87	-1.87	3.13	0.79	-3.58
2.60	3.30	0.50	0.25	6.76	7.26	-2.26	2.74	0.66	-4.12
2.80	3.40	0.40	0.16	7.28	7.68	-2.68	2.32	0.53	-4.62

The mean values of k_1 and k_2 , calculated by the method of least squares, are as follows:

$$k_1 = 2.84 \cdot 10^{-3}; k_2 = 6.80 \cdot 10^{-4}; k_1/k_2 = 4.2.^{\circ}$$

The dissociation constants of cis-[Pt(glh)₂(NH₃)₂]Cl₂ were determined analogously under the same conditions ($a = 5 \cdot 10^{-3}$ mole/liter in 0.5 M NaNO₃ solution):

$$k_1 = 3.4 \cdot 10^{-3}; k_2 = 6.10 \cdot 10^{-4}; k_1/k_2 = 5.6.$$

In these experiments the accuracy of the determination of k_1 was approximately $\pm 20\%$ and k_2 , $\pm 10\%$.

We also titrated 0.01 M solutions of the isomers of [Pt(glh)₂(NH₃)₂]Cl₂ with alkali in 0.1 M NaNO₃, as the use of a lower concentration of base electrolyte should lead to an increase in the difference in the successive dissociation constants. The following values were obtained:

$$\text{for trans-isomer } k_1 = 6.1 \cdot 10^{-3}; k_2 = 9.5 \cdot 10^{-4}; k_1/k_2 = 6.4;$$

$$\text{for cis-isomer } k_1 = 14.3 \cdot 10^{-3}; k_2 = 10 \cdot 10^{-4}; k_1/k_2 = 14.$$

During the titration of a 0.01 M solution of trans-[Pt(glh)₂(NH₃)₂]Cl₂ with alkali, a white precipitate of difficultly soluble [Pt(glh)₂ · (NH₃)₂]^{••} formed at the end of the experiment and this was analyzed for Pt.

Found %: Pt 51.62, [Pt(glh)₂(NH₃)₂]. Calculated%: Pt 51.73.

The dependence of k_1 and k_2 on the experimental conditions may be explained on the one hand by the effect in the change in ionic strength and on the other, especially in the case of k_1 , by its quite high value, so that in dilute solutions dissociation in the first stage may not obey the law of mass action. This was observed by Speakman [4] in the case of oxalic acid ($k_1 = 5 \cdot 10^{-2}$), where the thermodynamic dissociation constant k_1 was constant only in solutions whose concentrations exceeded 0.005 M.

The values of k_1 for oxalic acid given by different authors disagree considerably [5].

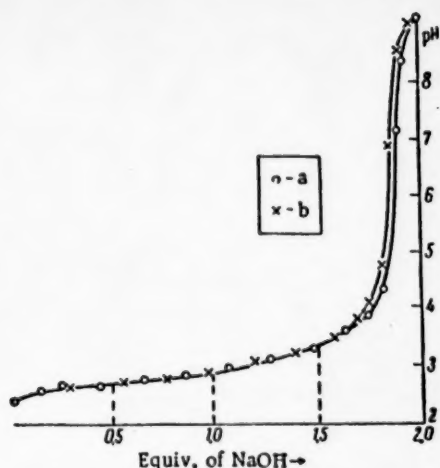
The data obtained show that the ions [Pt(glh)₂(NH₃)₂]²⁺ are quite strong acids with similar successive dissociation constants with either the two isomers having practically identical dissociation constants (in 0.005 M solution) or the acid properties of the cis-isomer in more concentrated solution somewhat exceeding the acid properties of the trans-isomer.

^{••} Within the given limits of accuracy, the dissociation constants calculated by the method of least squares agree with the constants found as the arithmetic means from the formulas:

$$k_1 = \frac{X_1 - X_2}{Y_1 - Y_2}, k_2 = \frac{X_2 Y_1 - X_1 Y_2}{X_1 - X_2}$$

for a series of points on the titration curve.

^{••} gl represents the ion NH₂CH₂COO⁻.



Curves of the potentiometric titration of 0.005 M solution of trans (a) and cis (b) isomers of $[\text{Pt}(\text{gly})_2(\text{NH}_3)_2]\text{Cl}_2$ in 0.5 M NaNO_3 solution with 0.195 N NaOH solution.

As amino acids are strong acids according to Bjerrum, with $\text{pK} = 2.33$, which corresponds to the dissociation of the ion $\text{NH}_3\text{CH}_2\text{COOH}^+$, it may be stated that their coordination both with the H^+ ion and the Pt^{2+} ion does not lead to strengthening of their acid properties since $\text{pK}_1 = 2.2-2.5$ for $[\text{Pt}(\text{gly})_2(\text{NH}_3)_2]^{2+}$. An insignificant increase in dissociation under the influence of the charge of the central ion is also observed for the somewhat more weakly dissociated ions HC_2O_4^- , for which $k_2 = 4.9 \cdot 10^{-5}$, while for trans- $[\text{Pt}(\text{HC}_2\text{O}_4)_2(\text{NH}_3)_2]$ $k_1 = 6.3 \cdot 10^{-4}$ [6]. If we have a very slightly dissociated addend such as H_2O , which has a dissociation constant of $1.8 \cdot 10^{-16}$, then in the state of coordination with Pt^{2+} , its dissociation constant increases to $4.8 \cdot 10^{-5}$.

The geometric structure of isomers normally has an effect on their acid properties; thus, cases are known where, due to interaction of the protons in the coordinated groups, the acid properties of the cis-isomer exceed those of the trans-isomer, as in unsaturated dibasic organic acids and the complex ions $[\text{Pt}(\text{NH}_2\text{OH})_2(\text{NH}_3)_2]^{2+}$, $(\text{PtPn}_2 \cdot \text{Cl}_2)^{2+}$ (where Pn is propylenediamine) [7]. The acid dissociation constant of the coordinated addend in these cases is appreciably lower than for glycine, for example; for cis- $[\text{Pt}(\text{NH}_2\text{OH})_2(\text{NH}_3)_2]^{2+}$ $k_1 = 3.3 \cdot 10^{-8}$, $k_2 = 6.6 \cdot 10^{-11}$.

In other cases where there is a strong trans effect by the addends, it leads to strengthening of the acid properties of the trans-isomer. This is observed with the ions $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ [8], $[\text{Co}(\text{En})_2(\text{H}_2\text{O})_2]^{3+}$ [9], and $[\text{Cr}(\text{En})_2(\text{H}_2\text{O})_2]^{3+}$ [10], where En is ethylenediamine. The similarity in the acid properties of the cis- and trans-isomers of $[\text{Pt}(\text{gly})_2(\text{NH}_3)_2]\text{Cl}_2$ we investigated may be explained by the fact that with strong dissociation of the addends, both the steric effects of the interaction of protons, which is connected with the cis- and trans-configurations, and the trans effect cease to be the determining factors.

Naturally, when the addends have strong acid properties both the phenomenon of coordination and the effects of the internal reaction of the addends in the complex have little effect on the magnitude of their acid dissociation.

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF BALTIC OIL SHALES

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With respect to its origin, composition, and properties, the Baltic shale kuckersite occupies a special position among caustobioliths [1]. Contemporary opinions on the chemical nature of the kerogen of kuckersite and the nature of the conversions during its thermal decomposition are very contradictory.

The presence of a considerable amount of heteroatomic functional groups in the kerogen and the high content of phenols in their thermal decomposition products have led some investigators to adopt a hydroxyaromatic structure for the organic material of kuckersite [2, 3]. Other authors consider that the basis of the kerogen macromolecule consists of closed polymethylene structures, which are converted to hydroxyaromatic rings on heating [4]. The thermal decomposition of the kerogen of kuckersite is then treated either as a chain of successive "primary" conversions [5] or is regarded as a complex of successive and parallel primary and secondary reactions [6].

These ideas, which are complicated as a result of indirect chemical analysis studies, could be substantially refined and extended by studying phenomena which directly characterize the molecular composition and structure of the kerogen and its thermal decomposition products. In particular, in the present article we present the results of the first stage in the study of the electron paramagnetic resonance (epr) of raw and thermally treated oil shale. The main purpose of the investigation was to obtain the qualitative characteristics of the epr spectrum of the test samples.

Samples and Investigation Procedures

The first series of samples consisted of three batches of kuckersite from the Kiviylü mining field of the Estonian deposit with various kerogen contents (concentrate, a mixture of shale from layers A-E from the workable part of the seam, and unenriched shale from layer A¹ with a high content of aluminosilicates in the mineral part). For comparison, we also included a sample of dictyonemic Estonian oil shale, whose kerogen apparently has a condensed aromatic structure with a high thermal stability [1].

The second series of samples consisted of kuckersite that had been ground to a grain size of 3-5 mm (a mixture from layers A-E) and heated to a given temperature (280, 360, 380, 420, 430, 450, 475, and 520°C) at a constant rate of 13°C per min and then kept at constant temperature for a given time. The design of the reactor guaranteed uniform heating of the fuel layer throughout the volume and brief contact between the volatile and solid materials, which limited the distorting effect of secondary reactions in the vapor phase [7]. We also studied the products from benzene extraction of some samples of thermally treated shale, namely solid residue and extracted primary bitumen. The characteristics of the samples and the results of the investigation are given in Tables 1 and 2; the composition of the mineral part of unenriched shales, which does not vary much, has been described in literature [8].

The epr spectra were plotted on an instrument of normal construction for recording derivative epr spectra with a sensitivity of approximately 10^{14} spins, calibrated against diphenylpicrylhydrazyl, and with an ÉPP-09 recorder by the procedure described in [9] at 20° and in some cases at -196°C with the ampoule and resonator cooled in liquid nitrogen. The results of the latter measurements will be given in a separate communication. The solid samples were ground to pass sieve No. 100 and the highly viscous thermal bitumen was dissolved in a twofold amount of benzene.

TABLE 1

Characteristics and Results of Investigation of Solid Samples

Sample No.	Material	Composition of mineral part, wt. %		Content of organic part, wt. %	Specific resistance, ohm · cm		Intensity of epr signal, arbitrary units	Duration of isothermal heating, min	Mol. wt. of tar
		Ac	CO ₂		a.c., 100 v	d.c., 500 v			
Series 1. Raw shale									
1	Enriched kuckersite	8,73	2,19	89,88	2,5 · 10 ⁹	6,8 · 10 ⁷	28		
2	Kuckersite, mix from layers A-E	46,59	14,96	38,45	1,68 · 10 ¹⁰	2,3 · 10 ⁸	17		
3	Kuckersite from layer A ¹	57,65	18,06	24,08	1,5 · 10 ¹⁰	1,8 · 10 ⁸	10,5		
4	Dictyonemic oil shale	80,35	—	19,65	4,0 · 10 ¹⁰	3,0 · 10 ⁸	18,5		
Series 2. A Thermally treated kuckersite from sample 2									
5	Shale heated to:								
	280°	48,75	17,21	34,04	9,8 · 10 ¹¹	5,5 · 10 ¹⁰	25	120	
6	360°	50,29	19,07	30,64	3,1 · 10 ¹¹	2,0 · 10 ¹⁰	42	60	
7	380°	50,57	18,61	30,82	3,0 · 10 ¹¹	1,6 · 10 ¹⁰	43,5	30	
8	420°	57,60	19,80	22,54	3,35 · 10 ¹¹	1,8 · 10 ¹⁰	136,5	20	
9	430°	57,36	20,09	22,55	—	5,1 · 10 ¹⁰	118,0	20	
10	450°	59,85	20,71	19,44	6,5 · 10 ¹¹	4,7 · 10 ¹⁰	99,0	0	208
11	450°	61,75	21,99	16,26	5,3 · 10 ¹¹	4,2 · 10 ¹⁰	108,0	15	215
12	450°	64,45	23,01	12,54	4,4 · 10 ¹¹	3,6 · 10 ¹⁰	162,0	30	221
13	475°	64,95	23,06	11,09	—	2,6 · 10 ¹⁰	129,5	0	175
14	475°	66,88	23,45	9,67	—	2,2 · 10 ¹⁰	193,0	15	183
15	520°	68,54	23,17	8,29	—	3,4 · 10 ⁹	207,0	0	224
16	520°	68,79	24,61	6,60	—	5,3 · 10 ⁸	216,0	15	223
B. Solid residue after extraction									
17	Shale residue								
	360°	50,33	18,15	31,52			48,5		
18	380°	52,16	18,12	29,72			60,0		
19	420°	60,26	19,84	19,90			141,0		

TABLE 2

Characteristics of Thermal Bitumens

Sample No.	Material	Elementary composition, wt. %			Mol. wt.	Intensity of epr signal, arbitrary units	Yield from kerogen, wt. %
		C	H	O + N + S			
20	Shale extract at:						
	360°	79,65	14,30	6,05	930	3,5	4,1
21	380°	82,66	10,98	6,36	818	5,0	12,4
22	420°	84,74	10,57	4,69	750	34,0	30,5

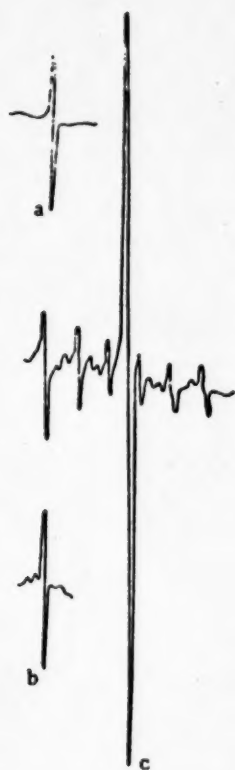


Fig. 1. Epr spectrum of concentrate (a), dictyonemic shale (b), and unenriched oil shale (c).

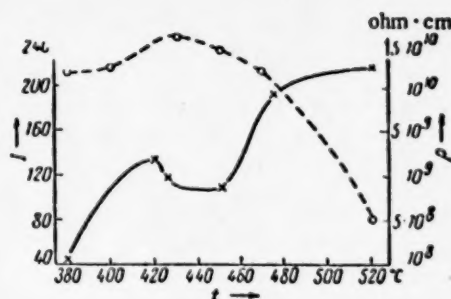


Fig. 2. Curves of the relation of the epr signal intensity, expressed in arbitrary units, and the specific electrical resistance to the temperature of isothermal heating of shales.

Main results. The epr spectrum plotted at 20° for the concentrate (Fig. 1a) showed a comparatively intense signal with a factor $g = 2.002$, a half-width $\Delta H = 0.6$ gauss, and $\sim 10^{17}$ unpaired spins. Dictyonemic shale also showed a narrow but quite intense signal (Fig. 1b) similar to the spectrum of diphenylpicrylhydrazyl. In this case $g = 2.02$ and $\Delta H = 0.6$ gauss.

As is known, polyconjugated and aromatic structures show a narrow, single-component signal with a g factor equal to that of a free electron.

The epr spectrum obtained for the concentrate confirms the hypothesis that there is considerable condensation of the kerogen in kuckersite, but does not give an unequivocal answer on the nature of its structure.

Unenriched shale (samples 2 and 3) and also samples 5-16 (Table 1), which had been subjected to thermal treatment, gave a seven-component signal with $\Delta H = 55$ gauss (see Fig. 1c). Enrichment of the shale led to the removal of those systems which gave the multicomponent signal, which were apparently of mineral origin (in all probability, Mn compounds).

The structure of these signals remained unchanged over the whole temperature range used.

As the epr spectra of samples of series 2 were mainly examined qualitatively, in Table 1 we give the results of an approximate comparison of the intensities of the epr signals expressed in arbitrary units, and the specific resistance in ohm·cm.

With an increase in the temperature of isothermal heating from 280 to 360°, the intensity of the signals for shale that had been heated for 120-130 min increased very slightly. There was a sharp increase in the intensity of the epr signal for a sample that had been heated at 420°. Since the intensity of the epr signals depended both on the heating temperature t and on the isothermal heating time τ , in Fig. 2 we give a curve of the relation $I = I(t)$ at $\tau = \text{const.}$

As Fig. 2 shows, the curve of this relation has two inflections in the temperature regions of $\sim 420^\circ$ and $\sim 450^\circ$.

This curve confirms the opinion that one of us expressed previously [6] that secondary reactions play a part in the thermal decomposition of shale. Figure 2 also gives a curve showing the relation of the specific resistance of the material to the isothermal heating temperature and it is antitatic to the epr curve as usually occurs over some temperature range for polyconjugated systems.

The epr spectra for the solid residue after extraction showed a picture which was apparently analogous to that described above. However, with an increase in t from 360 to 380°, the intensity of the signals increased somewhat more than for samples 6 and 7. The intensity of the signals for this group of samples at all values of t appear somewhat higher than for unextracted material. This means that in the solid residue after theoretically complete removal of the primary decomposition products that are distillable under the given conditions, there probably remains the most chemically condensed part of the decomposed kerogen and the observed epr spectrum is connected with this. This part is the initiator in the formation of the condensed part of the heavy tar and even more condensed coke; under the given conditions, active coke formation apparently begins at 430-440°.

On the basis of Table 1, it is also possible to follow the kinetic growth of the epr signal at $t = 450^\circ$. At $\tau = 0$, $I = 99.0$; and at $\tau = 15$ and 30 min, $I = 108$ and 162, respectively.

The data given on the values of I refer to the total solid residue, but the organic part in it decreases with an increase in t and τ , and therefore the actual increase in the intensity of the epr signals is much greater.

Data for bitumens are given in Table 2.

The epr spectra for the extracted mixture of primary products (bitumens) show a considerable reduction in the intensity of the epr signal for low-temperature bitumens in comparison with the total thermally treated material; the intensity of the signals increased with a change from $t = 360^\circ$ to 420° . Nonetheless, a very characteristic indication of secondary reactions even at a relatively low temperature and a low degree of decomposition of the kerogen is the small, but quite evident, increase in the intensity of the signals for low-temperature bitumen with a rise from 360 to 380°. It should also be noted that the intensity of the signals for bitumen dissolved in benzene had not fallen three days after solution.

A comparison of the qualitative data obtained with results of studying epr in various coals [10-12] indicates the considerably lower thermal and chemical stability of the kerogen in kuckersite and the active role of secondary condensations even when the shale is heated at a comparatively low temperature.

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SYNTHESIS AND PROPERTIES OF TETRA-n-PROPYLDIBORANE AND TETRA-n-BUTYLDIBORANE

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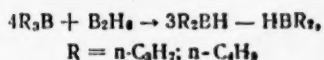
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The gas-phase reaction of trimethylboron and diborane forms mono-, di-, tri-, and tetramethyldiborane [1] with a 2.8% yield of the latter. Triethyldiborane and tetraethyldiborane were obtained analogously from triethylboron and diborane (8:1) [2] and n-propyl- and unsymmetrical di-n-propyldiborane were synthesized by this method from tri-n-propylboron [2]. Tetra-n-propyldiborane was obtained by the action of lithium aluminum hydride on di-n-propylboron chloride [3]. All known alkylidiboranes have been identified only through the vapor pressure. According to literature data, the stability of alkylidiboranes increases with an increase in the number of substituents though they all disproportionate at room temperature to an equilibrium mixture.

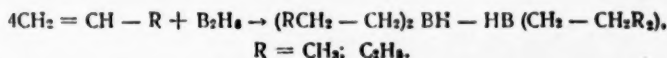
We investigated the reaction of diborane with trialkylborons (tri-n-propylboron and tri-n-butylboron) in ether and found that passing 1 mole of diborane into an ether solution of 4 moles of trialkylboron at room temperature yielded the tetraalkyldiboranes tetra-n-propyl- and tetra-n-butyldiboranes in a yield of 70-85%.



If an equimolecular amount of diborane was passed into an ether solution of tri-n-propylboron, distillation of the reaction products yielded unsymmetrical di-n-propyldiborane together with tetra-n-propyldiborane.

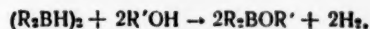
The second method of synthesizing tetraalkyldiboranes that we investigated was based on the reaction between diborane and olefins. This reaction, which was discovered by Hurd [4], is catalyzed by ethers [5] and has been used for the preparation of trialkylborons up to now.

We established that in ether at -70 to -30° diborane and olefins (propene and 1-butene) in a ratio of 1:4 form tetraalkyldiboranes in 48% yield.

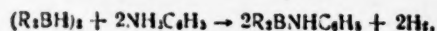


The tetraalkyldiboranes we synthesized were quite stable compounds which withstood heating to 100° and could be vacuum distilled. Their refractive index increased somewhat on standing after distillation. However, when the product was heated or distilled, the refractive index again fell to the initial value. Determination of the molecular weight in benzene indicated their partial dissociation to dialkylborane in solution.

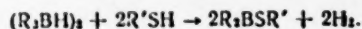
Tetraalkyldiboranes were spontaneously inflammable in air and had a high reactivity. They reacted with alcohols to form dialkylboric esters



with aniline to form dialkylphenylaminoborons.

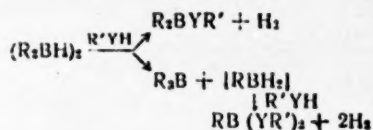


and with mercaptans to form dialkylthioboric esters



The reactions of tetraalkyldiboranes with various reagents are convenient preparative methods for synthesizing organoboron compounds. In most cases they are accompanied by the formation of only insignificant amounts of by-products. Thus, the action of *n*-butyl mercaptan on tetra-*n*-propyldiborane yielded only a small amount of *n*-propylthioboric ester together with di-*n*-propylthioboric ester. The reaction of tetra-*n*-butyldiborane with glycol was more complicated and yielded approximately equal amounts of the di-*n*-butylboric and *n*-butylboric esters of glycol together with tri-*n*-butylboron. The formation of the latter indicates that under the action of nucleophilic reagents, tetraalkyldiboranes undergo not only replacement of hydrogen atoms, but also disproportionation to trialkylborons and alkylboranes.

In the general form, the process may be represented by the following scheme:



The alkylborane arising under the action of the nucleophilic reagent forms an organoboron compound with one radical at the boron atom, while the trialkylboron remains unchanged (for example, in the reaction with glycol) or reacts to form, for example, a dialkylthioboric ester with a mercaptan [6]. As a result of the latter reaction, the gaseous products from the reaction of tetra-*n*-propyldiborane with a mercaptan were found to contain not only hydrogen, but also a small amount of propane.

Tetraalkyldiboranes are capable of reacting with olefins to form trialkylborons, and this method may be used to prepare unsymmetrical trialkylborons.

EXPERIMENTAL

All operations were carried out in an atmosphere of dry nitrogen. Diborane was obtained in 65-75% yield by adding an ether solution of boron trifluoride etherate to a suspension of sodium borohydride in ether.

Synthesis of Tetraalkyldiboranes

Tetra-*n*-butyldiborane. a) Into a continuously stirred solution of 18.2 g (0.1 mole) of tri-*n*-butylboron (b. p. 109°/20 mm, n_D^{20} 1.4260, d_4^{20} 0.7556) in 45 ml of dry diethyl ether was passed 0.0275 mole of diborane over a period of 2-3 hr. The ether was then removed in a water-pump vacuum and the residue subjected to fractional distillation. We obtained 17 g of tetra-*n*-butyldiborane with b. p. 40-41°/0.25 mm, n_D^{20} 1.4375, d_4^{20} 0.7647. The yield was 86.8% of theoretical.

Found %: C 76.26; H 15.04; B 8.75; H_{act} 0.82. $C_8H_{18}B$. Calculated %: C 76.22; H 15.19; B 3.58; H_{act} 0.791.

Molecular weight: found 216, calculated 252.

b) Over a period of 4 hr, 0.075 mole of diborane was passed into a continuously stirred solution of 0.375 mole of 1-butene in 100 ml of dry diethyl ether at -30°. The solvent was removed and the residue fractionated in vacuum. We obtained tetra-*n*-butyldiborane with b. p. 40-42° at 0.25 mm and n_D^{20} 1.4352. The yield was 45% of theoretical.

Tetra-*n*-propyldiborane. a) Into an ether solution of 28.4 g (0.203 mole) of tri-*n*-propylboron (b. p. 48°/13 mm, n_D^{20} 1.4148) was passed 0.055 mole of diborane. After removal of the ether, the reaction products were distilled. We obtained 20.4 g of tetra-*n*-propyldiborane with b. p. 33-34° at 1 mm, n_D^{20} 1.4327, d_4^{20} 0.7388. The yield was 70% of theoretical.

Found %: C 73.13; H 15.40; B 11.11; H_{act} 0.729. $C_6H_{15}B$. Calculated %: C 73.53; H 15.43; B 11.04; H_{act} 0.736.

b) Into a solution of 0.375 mole of propene in 100 ml of ether at -50° was passed 0.075 mole of diborane. After removal of the ether, the residue was fractionated in vacuum. Fractions were obtained: 1) $20-34^\circ/1.2$ mm, 4.7 g, n_D^{20} 1.4180; 2) $34-36^\circ/1.2$ mm, 7.4 g, n_D^{20} 1.4311; 3) In a trap cooled to -70° we collected 4.6 g of a substance with n_D^{20} 1.4175. The second fraction was tetra-n-propyldiborane (45% yield).

Synthesis of 1,1'-di-n-propyldiborane. Over a period of 3 hr, 0.12 mole of diborane was passed into a solution of 15.5 g (0.111 mole) of tri-n-propylboron in 100 ml of ether. After removal of the solvent in vacuum, the residue was subjected to fractional distillation. We obtained: 1) 2.9 g of a substance with b. p. $33-34^\circ/32$ mm, n_D^{20} 1.4088, which corresponded in analysis data and chemical properties to unsymmetrical di-n-propyldiborane (16% yield); 2) 6.5 g of tetra-n-propylborane with b. p. $33-34^\circ/1$ mm, n_D^{20} 1.4327.

Action of n-butanol on 1,1-di-n-propyldiborane. To 2.8 g of 1,1-di-n-propyldiborane was added 9.5 ml of n-butanol dropwise. There was vigorous evolution of hydrogen (2.15 liters). Distillation of the reaction products yielded: 1) 3.8 g of n-butyl di-n-propylborate with b. p. $72-76^\circ/7$ mm, n_D^{20} 1.4130 (literature data: b. p. $66.5^\circ/5$ mm, n_D^{20} 1.4133 [7]); 2) 3.8 g of tri-n-butyl borate with b. p. $72-74^\circ/2$ mm, n_D^{20} 1.4088; d_4^{20} 0.8572 (literature data: b. p. $105-106^\circ/8$ mm, n_D^{20} 1.4080; d_4^{20} 0.8567 [8]).

Reactions of tetraalkyldiboranes with alcohols. To 7.3 g of tetra-n-propyldiborane was added 5.8 g of n-butanol dropwise. Fractional distillation yielded: 1) 8.1 g of n-butyl di-n-propylborate (63%) with b. p. $59-63^\circ/4.5$ mm, n_D^{20} 1.4140 (literature data: b. p. $76-76.5^\circ/15$ mm, n_D^{20} 1.4133 [7]); 2) 2.1 g of di-n-butyl n-propylborate with b. p. $64-72^\circ/4.5$ mm, n_D^{20} 1.4130 (literature data: b. p. $83^\circ/7$ mm, n_D^{20} 1.4129 [9]). Hydrogen (1.58 liter) was obtained in the experiment. Analogously, from 10.5 g of tetra-n-butyldiborane and methanol we obtained 8.45 g (65%) of methyl di-n-butylborate with b. p. $90-91^\circ/42$ mm, n_D^{20} 1.4180, d_4^{20} 0.7845; MR found 50.11, calculated 49.57.

Found %: C 69.26; H 13.51; B 7.00. $C_9H_{21}BO$. Calculated %: C 69.23; H 13.46; B 7.05.

Reaction of tetra-n-butyldiborane with ethylene glycol. To 10.5 g of tetra-n-butyldiborane at room temperature was added 2.8 g of ethylene glycol. The reaction, which was accompanied by hydrogen liberation, continued for 7 hr. Fractional distillation yielded: 1) 3.25 g of ethylene n-butylborate with b. p. $80-81^\circ/66$ mm, n_D^{20} 1.4140 (literature data: b. p. $78-79^\circ/66$ mm, n_D^{20} 1.4129 [10]); 2) 4.4 g of tri-n-butyl borate with b. p. $64-67^\circ/3$ mm, n_D^{20} 1.4260; and 3) 4.67 g of ethylene di-n-butylborate with b. p. $155-156^\circ/3$ mm, n_D^{20} 1.4350 (literature data: b. p. $133-134^\circ/1$ mm, n_D^{20} 1.4340 [10]).

Reactions of tetraalkyldiboranes with aniline. To 12 g of tetra-n-propyldiborane was added 12 g of aniline dropwise. A white complex formed and this gradually decomposed with the liberation of hydrogen. Distillation yielded 18.5 g (80%) of di-n-propylphenylaminoboron with b. p. $120-123^\circ/11.5$ mm, n_D^{20} 1.5049 (literature data: b. p. $117.5^\circ/11$ mm, n_D^{20} 1.5050 [6]) and 1.3 g of a fraction with b. p. $90-174^\circ/1$ mm. Analogously, from 7 g of tetra-n-butyldiborane and 5.6 g of aniline we obtained 9.14 g (76%) of di-n-butylphenylaminoboron with b. p. $142-144^\circ/8.5$ mm, n_D^{20} 1.5003. Literature data: b. p. $139^\circ/7.5$ mm, n_D^{20} 1.5001 [11]. Hydrogen (1155 ml) was obtained in the experiments.

Reactions of tetraalkyldiboranes with mercaptans. To 7.1 g of tetra-n-propyldiborane was added 6.8 g of n-butyl mercaptan. Gases were liberated during the reaction. We obtained 1.59 liters of H_2 and 95 ml of propane. Distillation yielded 11.2 g (83%) of n-butyl di-n-propylthioborate with b. p. $98.5-102^\circ/11.5$ mm, n_D^{20} 1.4850 (literature data: b. p. $98.2^\circ/11$ mm, n_D^{20} 1.4590 [10]), and 1.4 g of di-n-butyl n-propylthioborate with b. p. $109-110^\circ/2$ mm, n_D^{20} 1.4895 (literature data: b. p. $150^\circ/13$ mm, n_D^{20} 1.4956 [12]).

Analogously, from 8.05 g of tetra-n-butyldiborane and 8 g of n-butyl mercaptan we obtained 10.13 g (75%) of n-butyl di-n-butylthioborate with b. p. $137-141^\circ/18$ mm, n_D^{20} 1.4604 (literature data: b. p. $118.5^\circ/8$ mm, n_D^{20} 1.4548 [11]).

The action of 7 g of n-propyl mercaptan on 10 g of tetra-n-butyldiborane yielded 11.7 g (74%) of n-propyl di-n-butylthioborate with b. p. $122-126^\circ/18$ mm, n_D^{20} 1.4600, d_4^{20} 0.8310; MR found 65.79, calculated 65.98.

Found %: C 66.35, 66.16; H 12.64, 12.46; B 5.56, 5.70. $C_{11}H_{23}BS$. Calculated %: C 66.00; H 12.50; B 5.50.

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SPECTROPHOTOMETRIC INVESTIGATION OF AQUEOUS SOLUTIONS OF IODOPOLYVINYL ALCOHOL

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Iodine is known to give a blue color not only with starch or amylose, but also many other inorganic and organic compounds of various chemical structures. These include calcium [1] and zirconium [2] hydroxides, oleum [3, 4], potassium acetate [5], lanthanum [6-8] and praseodymium [9] basic acetates, substituted flavones [10] and coumarins [11], narseline [12], cortisone [13, 14], cholic acid [15], nylon, polyvinyl borate [16], benzamide, piperine [17], and many others.

In 1926 Frey and Stark [18] found that polyvinyl alcohol also gives a blue color with iodine. In 1933 Miller and Bracken [19] reported that a blue color is formed only with completely deacetylated polyvinyl alcohol, while alcohol containing 10% and more of polyvinyl acetate units gives a crimson color with iodine. In 1936, Gallay's work on the sorption of iodine by polyvinyl alcohol appeared [20]. Brief data on the preparation of iodopolyvinyl alcohol in solutions were given in patent literature [21].

Iodopolyvinyl alcohol together with starch iodide and iodoamylose are of particular interest as they have valuable biological properties [22] (antimicrobial and therapeutic action and are nontoxic). As was shown in [23], these properties of solutions of iodine and iodinated high polymers are connected with their color.

In view of this and the almost complete absence of experimental data on the reaction of iodine with polyvinyl alcohol from the literature, we decided to use the absorption spectra of aqueous solutions of iodopolyvinyl alcohol in the range of 220-800 m μ for studying this reaction.

EXPERIMENTAL

Solutions of iodopolyvinyl alcohol were prepared from polyvinyl alcohol produced by the "Polyvinyl Acetate" Factory (Erevan) and containing 2.9% of residual acetate groups. We prepared 0.5-1.0% solutions of iodopolyvinyl alcohol in doubly distilled water by the action of the calculated amount of iodine in potassium iodide solution. The iodine of chemically pure grade was sublimed twice. The spectrophotometric measurements were made at room temperature on an SF-4 spectrophotometer. We studied the addition of iodine to polyvinyl alcohol over the range of 0.05 to 4.3 g of I₂ per g of polyvinyl alcohol (Fig. 1). The curve obtained has the form of a Freundlich adsorption isotherm.

The electronic absorption spectrum of an aqueous solution of pure polyvinyl alcohol over the range of 220-800 m μ has one absorption band with a maximum at 278 m μ . The absorption band of an aqueous solution of iodopolyvinyl alcohol in the given range has four absorption bands with maxima at 226, 288, 350, and 620 m μ (Fig. 2). With an increase in the concentration of iodine in solution, the maximum at $\lambda = 620$ m μ in the absorption spectrum of a solution of iodopolyvinyl alcohol is displaced somewhat toward short wavelengths. The

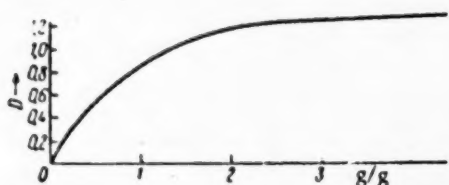


Fig. 1. Relation of optical density of iodopolyvinyl alcohol solutions with a constant polyvinyl alcohol concentration to the iodine concentration at $\lambda = 600 \text{ m}\mu$. Solution layer thickness 0.011 cm. Polyvinyl alcohol concentration 0.5 weight %.

of amylose, in the case of iodopolyvinyl alcohol solutions it was retained at a ratio of 0.0635 g of I_2 per g of polyvinyl alcohol.

The maximum at $\lambda \sim 600\text{--}620 \text{ m}\mu$ is observed in blue aqueous solutions of iodine in the presence of high polymers and is evidently connected with the center of the blue color. The maximum at $\lambda \sim 350 \text{ m}\mu$ is always observed in aqueous solutions of iodine with a yellow or red color. In the absorption spectra of blue aqueous solutions of iodopolyvinyl alcohol we investigated and also those of natural high polymers, the maximum at $\sim 620 \text{ m}\mu$ was inevitably accompanied by the maximum at $350 \text{ m}\mu$. To determine which color centers are connected with these two absorption maxima, we studied the absorption spectra of decolorized iodopolyvinyl alcohol solutions. After the blue color center had been destroyed by heating the iodopolyvinyl alcohol solution to 70° , the liquid acquired a yellow color. This color was subsequently retained when the solution was cooled to room temperature long enough for a spectrum to be plotted. As Fig. 3 shows, the absorption spectrum of the heated solution showed three maxima: at 226, 288, and $350 \text{ m}\mu$. Thus, destruction of the blue color center by heating led to the disappearance of the absorption maximum at $620 \text{ m}\mu$, while the maximum at $\lambda = 350 \text{ m}\mu$ was retained. When the solution was cooled, it again acquired a blue color and the maximum at $\lambda = 620 \text{ m}\mu$ again appeared in the absorption spectrum (Fig. 3).

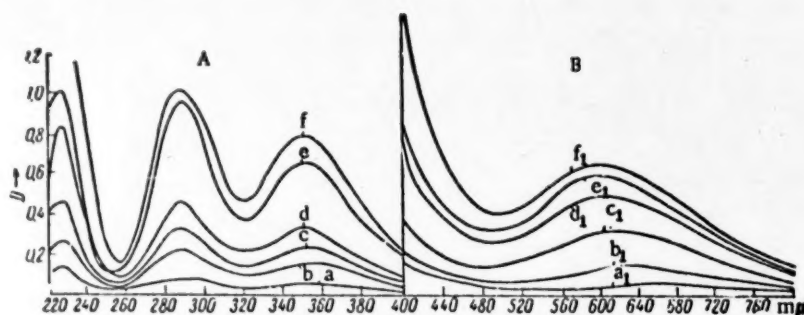


Fig. 2. Absorption curves of aqueous solutions of iodopolyvinyl alcohol. Solution layer thickness 0.0063 cm. A) polyvinyl alcohol concentration 0.1 weight %, C_{I_2} : a) 0.001 N; b) 0.002 N; c) 0.004 N; d) 0.008 N; e) 0.01 N; f) 0.016 N. B) polyvinyl alcohol concentration 0.5 weight %, C_{I_2} : a₁) 0.005 N; b₁) 0.01 N; c₁) 0.02 N; d₁) 0.04 N; e₁) 0.05 N; f₁) 0.08 N.

The yellow solution obtained by heating iodopolyvinyl alcohol solution was completely decolorized by the action of sodium thiosulfate, and the maxima at 288 and $350 \text{ m}\mu$ disappeared from its absorption spectrum. The maximum at $\lambda = 226 \text{ m}\mu$, which belongs to the hydrated anion I^- , was not only retained, but increased (Fig. 3), as was to be expected from the reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with iodine. A blue solution of iodopolyvinyl alcohol was instantaneously decolorized completely by the action of excess $\text{Na}_2\text{S}_2\text{O}_3$ and the absorption spectrum of this

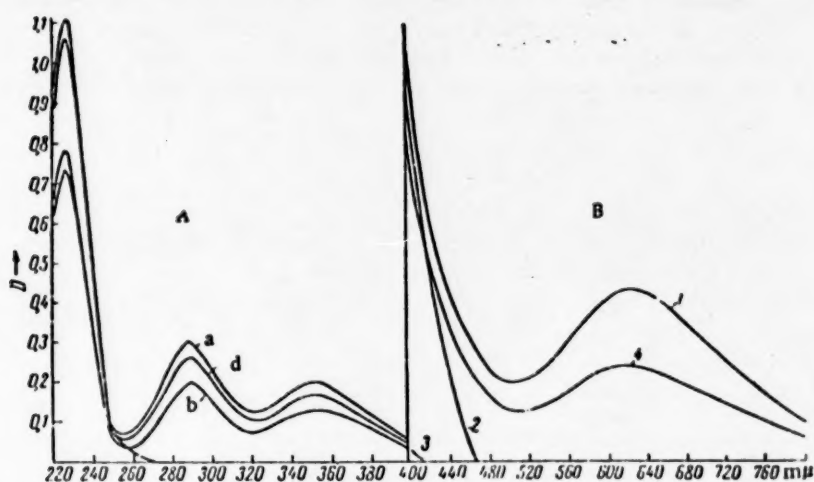


Fig. 3. Absorption curves of an aqueous solution of iodopolyvinyl alcohol decolorized by heating and by the addition of sodium thiosulfate. Polyvinyl alcohol concentration 0.05 weight %. Solution layer thickness: A) 0.0063 cm, B) 0.1 cm. a) Solution before decolorization; b) solution decolorized by heating; c) solution decolorized by addition of $\text{Na}_2\text{S}_2\text{O}_3$; d) solution decolorized by heating and color restored on cooling.

decolorized solution retained a single absorption maximum at $\lambda = 226 \text{ m}\mu$. In contrast to iodopolyvinyl alcohol solution decolorized by heating, a solution decolorized by sodium thiosulfate did not recover either a yellow or blue color.

Decolorization of a yellow aqueous solution of iodine involves the simultaneous disappearance from the absorption spectrum of the solution of the two maxima at 288 and 350 $\text{m}\mu$.

To determine the nature of these absorption maxima more accurately, we studied the absorption spectra of dilute aqueous solutions of ICl , and I_2 in cold potassium hydroxide solution. Both these solutions are yellow. The absorption spectra of these solutions contained a sharply expressed maximum at $\lambda = 350 \text{ m}\mu$, while the maximum at $\lambda \sim 288\text{--}290 \text{ m}\mu$ was completely absent. From this it follows that the yellow color of the given solutions is connected with the presence of the maximum at $\lambda = 350 \text{ m}\mu$ in the absorption spectrum, and the maximum at $\lambda \sim 288\text{--}290 \text{ m}\mu$ has no connection with the yellow color center. These data are in complete agreement with results obtained by studying absorption spectra of colorless aqueous solutions of KIO_3 and KIO_4 . These spectra show appreciable absorption only at $\lambda \sim 250 \text{ m}\mu$, which is connected with the anion IO_3^- as was shown previously by Awtrey and Connick [27]. The maximum at $\lambda = 350 \text{ m}\mu$ was completely absent from the absorption spectra of KIO_3 and KIO_4 solutions.

The absorption maximum at 226 $\text{m}\mu$, which belongs to the hydrated anion I^- , is present in the absorption spectrum of colorless solutions of iodides and has no connection with color centers in exactly the same way as the maximum at 288–290 $\text{m}\mu$, which belongs to the complex anion I_3^- . In our opinion, this explains why neither solutions of iodides [24] nor a solution of triiodide I_3^- [25, 26] show an antimicrobial action. The absorption maximum at 350 $\text{m}\mu$ belongs to IO^- , which participates in the formation of the color center of yellow aqueous solutions of iodine. The maximum at 620–625 $\text{m}\mu$ is connected with the color center characteristic of solutions of iodine in the presence of high polymers, including polyvinyl alcohol.

As was shown in [23], iodine incorporated in high polymers molecules has a higher antimicrobial effect than iodine in the form of IO^- . From this it follows that the blue color center has an independent antimicrobial effect in addition to the yellow color center. The antimicrobial action of blue solutions of iodinated high polymers is the result of the total action of IO^- and the blue complex. The destruction of these color centers with sodium thiosulfate with complete decolorization of the solutions is accompanied by the disappearance of the maxima at $\lambda \sim 350$ and $\sim 620 \text{ m}\mu$ from their absorption spectra and involves the complete loss of antimicrobial

activity. This conclusion is in agreement with data presented in [22, 23] on the properties of I^+ . The antimicrobial properties of compounds containing I^+ were used by one of us for producing therapeutic preparations. For example, iodopolyvinyl alcohol shows a positive therapeutic effect in such diseases as acute and chronic tonsillitis, ozena, otitis, candidiasis of the mucous membranes, dysentery, and a number of others and also as a blood substitute.

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INDOLE RING CLOSURE OF AZOBENZENE WITH CYCLOHEXANONE

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In investigating the decomposition of benzenediazonium fluoborate in various ketones, we established that in acetophenone, diethyl ketone, methyl butyl ketone, dipropyl ketone, and acetoacetic ester the decomposition proceeds wholly with the liberation of nitrogen. Reactions in tetralone and cyclopentanone led to almost complete liberation of nitrogen from the benzenediazonium, but in this case we also detected traces of aniline and ammonium fluoborate.

The decomposition of benzenediazonium in cyclohexanone and its methyl homologs proceeded quite differently. In this case there was no liberation of nitrogen. The benzenediazonium was reduced to phenylhydrazine, which formed cyclohexanone phenylhydrazone, which cyclized to tetrahydrocarbazole. The reaction was accompanied by the liberation of ammonium fluoborate, i.e., there was normal indole ring closure in this case.

In our previous work it was shown that azobenzene is reduced to hydrazobenzene by the hydride hydrogen of ketones and many other organic compounds [1]. In the reaction of azobenzene with cyclohexanone, as in the case of benzenediazonium, surprisingly there was also indole ring closure, tetrahydrocarbazole was formed, and aniline and not ammonia was liberated as in the classical Fischer-Arbuzov synthesis. The boron trifluoride-anisole complex was used as a catalyst.

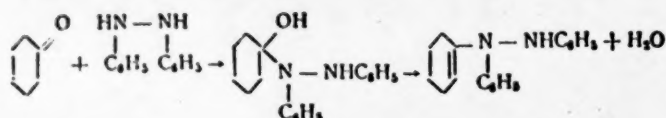
The use of boron trifluoride as a condensing agent in the Fischer indole synthesis has been described previously [2]. The reaction products from azobenzene and cyclohexanone also contained phenyl isonitrile (2%). Phenyl isonitrile was also obtained in very small amounts (2%) in the reaction of benzenediazonium fluoborate with cyclohexanone and acetone. Here there was apparently a new rearrangement whose nature has to be determined.

The formation of indole derivatives from azobenzene and benzenediazonium fluoborate evidently includes the initial stage of reduction to hydrobenzene and phenylhydrazine, respectively. If hydrazobenzene was used in the reaction with cyclohexanone instead of azobenzene, tetrahydrocarbazole was formed in the same yield as with azobenzene. It is interesting to note that despite the presence of boron trifluoride as a catalyst, there was no benzidine rearrangement in this case. In a blank experiment without cyclohexanone, hydrazobenzene in ether was instantaneously rearranged to benzidine when the boron trifluoride-anisole complex was added. In cyclohexanone, the rate of the Fischer indole rearrangement is apparently much greater than that of the benzidine rearrangement. In the case of azobenzene in such ketones as α -tetralone, dipropyl ketone, acetophenone, and cyclopentanone, only benzidine was obtained and no indole derivatives were detected. If BF_3 was replaced by sulfuric acid in the reaction of azobenzene with cyclohexanone, only the benzidine rearrangement occurred in cyclohexanone, also.

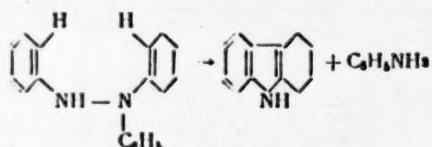
When boron trifluoride was replaced by cuprous chloride (Arbuzov synthesis of indoles), there was complete disproportionation of hydrazobenzene to form azobenzene and aniline and there was no further reaction.

The mechanisms of the reduction of benzenediazonium fluoborate and azobenzene in cyclohexanone and *p*- and *o*-methylcyclohexanones are probably the same. The reduction is produced by hydride hydrogen abstracted

from cyclohexanone or its methyl homologs. The hydrazobenzene formed reacts with the ketone to give the corresponding enehydrazine.



Diphenylcyclohexenylhydrazine cyclizes to form tetrahydrocarbazole by the mechanism proposed by G. and R. Robinson [3] and demonstrated by A. E. Arbuzov, Yu. P. Kitaev [4, 5], and N. N. Suvorov et al. [6]:



It is evident that in this case, as in Fischer's reaction [11], the nitrogen attached directly to the cyclohexane ring is eliminated.

EXPERIMENTAL

Reaction of Benzenediazonium Fluoborate with Ketones

With cyclohexanone. A solution of 10 g (0.052 mole) of benzenediazonium fluoborate in 50 ml of cyclohexanone was stirred for an hour at 40-50° (to a negative reaction with *B*-naphthol) and then for a further hour at 110-120°. The cooled reaction mixture was diluted with ether and filtered and the precipitate of ammonium fluoborate washed with ether. The yield was 2.8 g (51.8%, calculated on the benzenediazonium used for the reaction). The ether-cyclohexanone solution was washed free from aniline with dilute hydrochloric acid. The aniline was isolated as the benzoyl derivative in a yield of 0.8 g and this had m. p. 160-162°. The ether and cyclohexanone were removed by distillation and the residue vacuum distilled to yield two fractions: one with b. p. 95-104° (3 mm) (9 g), forming a thick oil with an odor of isonitrile; the other with b. p. 105-155° (3 mm) (2.1 g), forming a thick oil, which solidified to a white crystalline mass.

After being washed with ligroin, the crystalline tetrahydrocarbazole was pressed out (1.2 g, 13%); it had m. p. 114-115°; literature data [8]: m. p. 114°. A mixed melting point with authentic tetrahydrocarbazole was not depressed. Tetrahydrocarbazole picrate had m. p. 132-133°; literature data [8]: m. p. 132°.

The first fraction and filtrate from the second fraction were combined and washed with 10% sulfuric acid, the sulfuric acid extracts distilled, and the formic acid in the distillate was determined by boiling with mercuric chloride [9]. The yield was 2%, calculated on the benzenediazonium used for the reaction.

With o-methylcyclohexanone.* From the reaction mixture we isolated 5.25 g (96.9%) of ammonium fluoborate and 0.2 g of N-benzoylaniline. Vacuum distillation yielded 3 g of a light yellow oil, which contained nitrogen (Lassaigne's test) and had b. p. 132-150° (15 mm). The oil was dissolved in alcohol. From the alcohol solution we obtained 2.4 g of yellow 11-methyltetrahydrocarbazole picrate with m. p. 168-169°; literature data [1]: m. p. 169°.

Found %: C 55.07, 55.17; H 4.46, 4.27; N 13.62, 13.72. $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_7$. Calculated %: C 55.07; H 4.32; N 13.53.

From the mother solution we isolated 0.64 g of 1-methyltetrahydrocarbazole picrate with m. p. 145° (dark brown needles); literature data [10]: m. p. 145°.

Found %: C 55.25; H 4.56; N 13.85.

The total yield of methyltetrahydrocarbazoles was 0.0073 mole (14% on the benzenediazonium fluoborate taken for the reaction).

* The reaction was carried out under the conditions described for the experiment with cyclohexanone.

With *p*-methylcyclohexanone.* We obtained 3.8 g of ammonium fluoborate (70.3%) and 0.5 g of *N*-benzoylaniline. Vacuum distillation yielded 3.3 g of a thick oil, which contained nitrogen and had b. p. 150-180° (4 mm). From 1.1 g of this oil we obtained 0.7 g of 3-methyltetrahydrocarbazole picrate with m. p. 127-128° which was recrystallized from a mixture of ligroin and benzene (1:1).

Found %: N 13.77, 13.67.

The total yield of 3-methyltetrahydrocarbazole was 9.7% of theoretical.

With cyclopentanone.* Almost the whole of the benzenediazonium fluoborate was decomposed with the liberation of nitrogen. We isolated only 0.2 g of NH_4BF_4 and 0.3 g of *N*-benzoylaniline.

Reaction of Azobenzene with Ketones

With cyclohexanone. To 10 g (0.0549 mole) of azobenzene in 60 ml of cyclohexanone was added 10 ml of anisole containing 3 g (0.044 mole) of boron trichloride. The mixture was heated at 100-110° for 2.5 hr and then diluted with ether and washed with 5% hydrochloric acid. From the hydrochloric acid extracts we obtained 6.1 g (0.065 mole) of aniline with b. p. 175-180°. The cyclohexanone and its condensation products were distilled from the organic layer in vacuum and the residue was distilled with superheated steam. From the distillate we isolated 3.3 g (35.1%) of tetrahydrocarbazole.

With *p*-methylcyclohexanone.* From the hydrochloric acid extracts we isolated 0.7 g of benzidine sulfate and 2 g (0.0204 mole) of aniline. The methylcyclohexanone and its condensation products were distilled from the organic layer in vacuum and the azobenzene was steam distilled from the residue. The weight of the residual oil was 2.2 g. From 0.5 g of this oil we obtained 0.25 g of 3-methyltetrahydrocarbazole picrate with m. p. 127-128°, and a mixed melting point with 3-methyltetrahydrocarbazole picrate was not depressed. The total yield of the picrate was 1.1 g (0.00265 mole, 4.8% calculated on the starting azobenzene).

With α -tetralone.* From the reaction mixture we isolated only 3.2 g of benzidine sulfate (59.7% calculated on the azobenzene reacting). We recovered from the reaction 6.55 g of azobenzene.

With dipropyl ketone.* From the reaction mixture we obtained 1.3 g of benzidine sulfate (22.6%). We recovered 6.31 g of azobenzene from the reaction.

Reaction of Hydrazobenzene with Cyclohexanone

A mixture of 5 g (0.0271 mole) of hydrazobenzene (m. p. 122-123°), 50 ml of cyclohexanone, and 6 ml of anisole containing 1.6 g of boron trifluoride was boiled for 2.5 hr in a stream of nitrogen and treated as in the experiment with cyclohexanone. From the sulfuric acid extracts we isolated aniline, which was diazotized and coupled with *o*-naphthol. The yield of azo dye was 1.6 g (0.0064 mole) and it had m. p. 130-131°; literature data [11]: m. p. 131°. Distillation of the organic layer with superheated steam gave 1.4 g of tetrahydrocarbazole (0.0082 mole, 30.2% of theoretical).

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*The reaction was carried out under the conditions described in the experiment with cyclohexanone.

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EFFECT OF THE STRUCTURE OF ARYLHYDRAZONES ON THEIR CONVERSION TO INDOLE DERIVATIVES

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The discussion of the mechanism of the Fischer reaction has recently been revived [1, 2]. It may be considered quite accurately established as a result of investigations. However, the question of the effect of substituents in the arylhydrazone molecule on the yield of the indole derivative has not been studied adequately as yet.

One of us with V. K. Antonov [3] and V. P. Mamaev and L. B. Shagalov [4] showed clearly that there is an increase in the yield of the indole derivative when electron-donor substituents are introduced into the position para to the hydrazo group. Having a method [5] of separating the Fischer reaction into 3 stages in accordance with the mechanism of G. and R. Robinson [6], we decided to determine the changes in the arylhydrazone molecule and precisely the stage producing a favorable effect on the conversion of the latter into an indole derivative.

On acetylating a series of arylhydrazones (phenylhydrazones of acetaldehyde, propionaldehyde, acetone, methyl ethyl ketone, and cyclohexanone; the p-tolylhydrazone of methyl ethyl ketone; p-methoxyphenylhydrazones of acetaldehyde, acetone, and methyl ethyl ketone; and p-nitrophenylhydrazones of methyl ethyl ketone and cyclohexanone) with acetic anhydride in the presence of p-toluenesulfonic acid, in all cases apart from acetaldehyde we obtained the corresponding (N,N'-diacetyl- β -arylhydrazino)-alkenes. This is in complete agreement with the work of A. E. Arbuzov and Yu. P. Kitaev [7], who demonstrated experimentally that arylhydrazones are in tautomeric equilibrium with the corresponding enehydrazines.

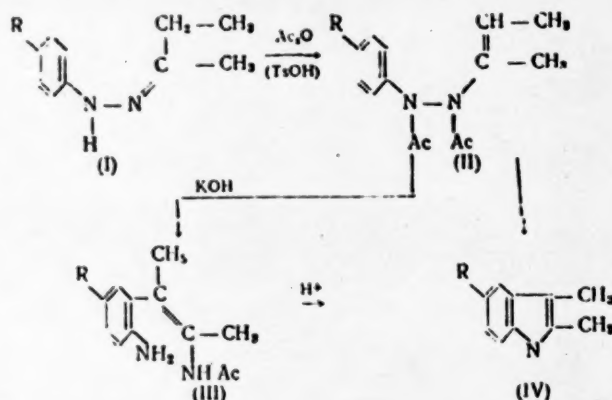
In the case of acetaldehyde phenylhydrazone and p-methoxyphenylhydrazone, the molecule was decomposed during acetylation with the formation of α,β -diacetylphenylhydrazine and N-acetyl-p-anisidine, respectively. However, it is known that acetaldehyde phenylhydrazone does not give indole under the conditions of the Fischer reaction. Much more interesting results were obtained on studying stage II of the Fischer reaction, namely the o-benzidine rearrangement.

Thus, hydrolysis of 2-(N,N'-diacetyl- β -phenylhydrazino)-2-butene (II, R = H) and its p-methyl derivative with aqueous sulfuric acid (1:1) gave 2,3-dimethyl- (or 2,3,5-trimethyl-) indole, and boiling with 5% aqueous alkali gave the o-benzidine rearrangement product, namely 3-acetylamino-2-(o-aminophenyl)-2-butene (III, R = H) [5] (or its methyl derivative). At the same time, this rearrangement did not occur in either case with 2-(N,N'-diacetyl- β -p-nitrophenylhydrazino)-2-butene (II, R = NO₂, m. p. 98-99°), and hydrolysis yielded p-nitrophenylhydrazine and methyl ethyl ketone.

Found %: C 58.10; H 5.78; N 14.65, 14.70; Ac 28.13, C₁₄H₁₇O₄N₃. Calculated %: C 57.73; H 5.84; N 14.43; Ac 28.80.

On the other hand, when heated for 2 hr with a 5% alcohol solution of potassium hydroxide, the analogous p-methoxy derivative (II, R = OCH₃, m. p. 65-66.5°) gave an 85% yield of 5-methoxy-2,3-dimethylindole (IV, R = OCH₃, m. p. 110-112°, λ_{max} 228 mμ, log ε = 4.35; λ_{max} 288 mμ, log ε = 3.95).

Found %: C 65.81; H 7.35; N 10.33, 10.66; Ac 31.3. C₁₅H₂₀O₃N₂. Calculated %: C 65.22; H 7.24; N 10.14; Ac 31.1.



These examples conclusively demonstrate that electron-acceptor groups hamper and electron-donor groups facilitate the o-benzidine rearrangement, and in the latter case, stage III, i.e., closure of the pyrrole ring, is also facilitated.

As it is well known that the introduction into the p-position of the aniline molecule of a methoxy group increases and a nitro group decreases the affinity of the nitrogen for a proton, with alkylation at the amino group, like the introduction of an electron-donor substituent, increasing the basicity of the amine, it seemed interesting to determine whether a similar substitution at the hydrazone nitrogen would affect the course of the Fischer reaction.

It is known that the yields of indole derivatives from asymmetric phenylalkylhydrazones are higher than from unsubstituted compounds [8]. We also showed previously that a methyl group has a positive effect on stages II and III of the reaction by means of our method [9]. However, in the literature there is the report of Perkin and Plant [10] on the conversion of the α-acetyl-α-phenylhydrazone of cyclohexanone into 9-acetyl-1,2,3,4-tetrahydrocarbazole, which would seem to indicate that the basicity of the nitrogen atom attached to the aromatic nucleus has no effect on the ease of the Fischer reaction. By repeating the work of the British investigators and obtaining the above phenylhydrazone directly from α-acetyl-α-phenylhydrazine and cyclohexanone, we showed that in this case the process involves the loss of the acetyl group and the formation of free (m. p. 117-119°) and not acetylated tetrahydrocarbazole.

Finally, a comparison of the instability of α-phenylhydrazine from acetaldehyde and the smooth formation of 1-(N,N'-diacetyl-β-phenylhydrazino)-1-propene (b. p. 142-145° at 2 mm) from propionaldehyde phenylhydrazone indicates that the latter is explained by the inductive effect of the terminal methyl group.

Found %: C 67.35; H 6.98; N 11.98, 12.13. C₁₃H₁₆N₂O₂. Calculated %: C 67.24; H 6.89; N 12.06.

The latter apparently also facilitates the o-benzidine rearrangement. In this respect it is interesting to note that the above enehydrazine rearranges when boiled with 5% alcoholic alkali to 1-acetyl-amino-2-(o-aminophenyl)-1-propene (m. p. 109-110.5°), which forms skatole when treated with hydrochloric acid.

Found %: C 69.22, 69.05; H 7.29, 7.44; N 15.03; Ac 22.61. C₁₁H₁₄O₂N. Calculated %: C 68.92; H 7.36; N 15.00; Ac 22.60.

At the same time, the isomeric 2-(N,N'-diacetyl-β-phenylhydrazino)-1-propene (m. p. 94-95°) from acetone phenylhydrazone does not undergo an o-benzidine rearrangement during alkaline hydrolysis, but is hydrolyzed to phenylhydrazine, though on boiling with aqueous sulfuric acid (1:1), it forms 2-methylindole.

Found %: C 67.34; 66.81; H 7.05, 6.95; N 11.92, 12.04; Ac 36.4. $C_{13}H_{16}O_2N_2$. Calculated %: C 67.24; H 6.89; N 12.06; Ac 37.0.

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CRYSTALLIZATION OF LOW-MOLECULAR SUBSTANCES FROM SOLUTIONS IN HIGH POLYMERS

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Supersaturated solutions with an anomalously high stability are readily formed during the solution of low-molecular substances in polymers. The crystallization of low-molecular substances from supersaturated polymer solutions occurs mainly at the polymer-gas boundary, in contrast to typical solutions in liquids. In technology, this phenomenon is known as blooming. The blooming of dissolved substances is an extremely undesirable phenomenon [1]. Despite the considerable amount of data published on this problem, the reason for blooming has not been found up to now.

In the present work we attempted to find the reason for this phenomenon from experimental material. As the subject of the investigation we chose the system sulfur-polybutadiene (SKB-30). To determine the relative amount of sulfur crystallizing on the surface of polybutadiene, we used the tracer method with S^{35} proposed by Auerbach and Gehman [2].

As the basic proportion corresponding to the supersaturation limit [3], we used 2 g of sulfur to 100 g of polybutadiene. Laboratory rollers were used for mixing. The samples studied, which were 26 mm in diameter and 2 mm thick, were pressed in cellophane in a press for 60 min at 100°. The cellophane was removed from one face of the sample before measurements. The activity of the samples was measured on the side that was not covered with cellophane with an end-window counter.

An investigation of the kinetics of blooming showed that even a day after the cellophane had been removed from the sample surface there was a considerable increase in the activity of the sample (Fig. 1). This is explained by crystallization of sulfur on the surface and its migration from the volume to the surface due to the concentration gradient arising.

Determination of the activity of samples covered with cellophane at various intervals after pressing showed that the activity of the samples did not increase in this case. With prolonged storage of the samples in a covered state, the intensity of blooming decreased (Fig. 1b) and the sample finally lost its capacity to bloom (Fig. 1c), i.e., equilibrium was reached due to crystallization in the volume. With crystallization on the surface, equilibrium was reached after 18-20 days for a sample 2 mm thick. It should be noted that in this case crystallization began almost immediately after removal of the cellophane, and the time for equilibrium to be reached was determined by the rate of diffusion of sulfur from the plate. With a plate thickness of 1 mm, equilibrium was reached after 10-12 days.

When there was no free surface, equilibrium was not reached even after 60 days, i.e., the rate of crystallization in the volume was considerably less than the rate of crystallization on the surface. Crystallization in the volume apparently involves overcoming obstacles which are absent in crystallization on the surface.

The process of crystallization is known to consist of two stages: the formation of nuclei and their subsequent growth. An investigation of the relation of the intensity of blooming to the concentration of the

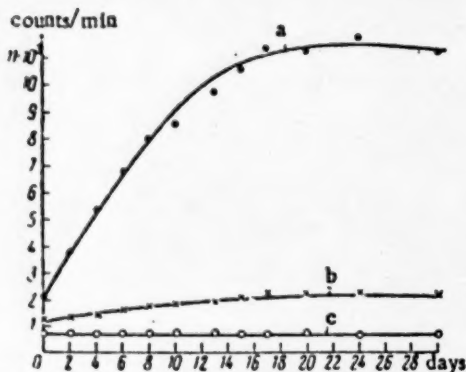


Fig. 1. Relation of activity of polybutadiene samples to time after removal of protective cellophane layer. Duration of storage of samples after pressing: in days: a) 1; b) 60; c) 135.

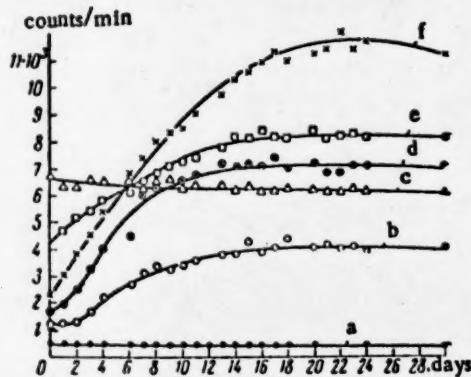


Fig. 2. Change in activity with time in relation to the sulfur concentration (in g per 100 g): a) 0.5; b) 1.2; c) 6.0; d) 1.5; e) 4.0; f) 2.0.

supersaturated solution showed that the obstacles encountered during crystallization in the volume were largely connected with the formation of crystallization nuclei. As the data presented in Figs. 2 and 3 show, the intensity of blooming first increased with an increase in the solution concentration and then fell. The absence of blooming at high sulfur concentrations (6 g and more per 100 g of polymer) indicates that there is rapid crystallization in the volume in this case. At high supersaturation there was an increase in the rate of both stages of the crystallization process. However, had the obstacles to crystallization in the volume been connected with the growth of crystals, then after the fall in the sulfur concentration to low degrees of supersaturation, the rate of crystallization should have decreased and the solution remained supersaturated for a long time.

Therefore, the fact that equilibrium was established rapidly at high degrees of supersaturation shows that the main obstacles were encountered in the formation of crystallization nuclei. Attempts to initiate crystallization by the introduction of fillers, namely carbon black, chalk, BaSO_4 , and Sb_2S_3 , did not give positive results. Only when powdered metallic selenium was introduced into the mixture was it possible to initiate crystallization in the volume, as was indicated by the absence of blooming.

Metallic selenium is insoluble in rubber. Selenium is isomorphous with sulfur and readily forms mixed crystals with it. Its introduction into the mixture was equivalent to the introduction of crystallization nuclei into a solution. This experiment confirms the conclusion drawn above.

The formation of crystallization centers occurs as a result of fluctuations in the concentration of the solute. Thereupon there first arise microregions with an amorphous structure [4] and as a result of molecular rearrangement, these are converted into centers for further development of the crystal. The presence of solvent molecules in these microregions hampers the formation of crystalline nuclei. It is evident that the time for the removal of solvent molecules from the microregion of nucleus formation depends on the coefficient of self-diffusion of the solvent molecule. On the other hand, the probability of the formation of a concentration fluctuation zone and its life time depend on the degree of supersaturation of the solution and the diffusion coefficient of the dissolved substance in the given solvent.

In the case of low-molecular solvents, the difference in the diffusion coefficient of the solute and the self-diffusion coefficient of the solvent is usually small. However, in the case of polymer solutions of low-molecular substances, it is quite considerable; for example, for rubbers the coefficient of self-diffusion at 2° is of the order 10^{-11} cm^2/sec [5], while the coefficients for the diffusion of low-molecular substances in rubber are of the order of 10^{-8} cm^2/sec [6]. Such a large difference in values characterizing the mobility of molecules indicates that the probability of the formation of crystallization centers in the volume at the same degree of supersaturation is considerably less with a polymeric solvent than with low-molecular solvents. In crystallization on a surface, the mobility of the solvent molecules is not the limiting factor, so that the probability of the formation of crystallization centers on the surface is considerably greater than in the volume of the polymer.

Structuralization and crystallization of a polymer produce a sharp decrease in the mobility of its molecules. The probability of crystallization in the volume should decrease considerably under these conditions. In actual

Sample No.	Free sulfur, %	Equilibrium modulus, kg/cm ²	Crystallization	
			with a free surface	without a free surface
1	1.48	10.1	Intense blooming after 3 days	Many crystals in volume after 10 days
2	1.51	19.2	Intense blooming after 7 days	No crystals formed in volume after 1 year

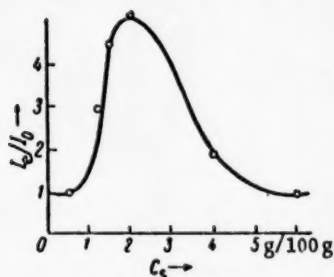


Fig. 3. Effect of concentration on blooming of sulfur from polybutadiene. I_0) initial activity; I_e) equilibrium activity of sample.

fact, in crystalline polycaprolactam the crystallization of the monomer proceeds rapidly when a free surface is present, while, when it is absent, a supersaturated solution does not break down even after several years. The table gives data on blooming and crystallization in the volume for synthetic butadiene rubber vulcanizates with different densities of the three-dimensional lattice.

The increase in the mobility of the molecules of polymer due to plasticizing of the latter with low-molecular liquids should increase the probability of crystallization in the volume. In actual fact, it is known that blooming does not occur with oily rubbers [2].

The examples presented confirm the accuracy of the conclusion that the obstacles to crystallization in the volume are caused by the low mobility of the solvent molecules.

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SYNTHESIS AND SOME CONVERSIONS OF SECONDARY γ -SILICON-CONTAINING ACETYLENIC ALCOHOLS

Corresponding Member Academy of Sciences of the USSR

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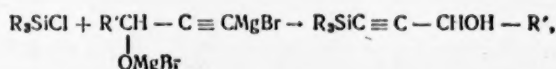
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In our previous investigations [1-3] a method was developed for preparing primary and tertiary silicon-, tin-, and germanium-containing acetylenic alcohols. A study of the chemical properties of these compounds showed that they are very reactive substances. Their chemical properties are reminiscent of those of their organic analogs, but they also differ considerably from the latter and show a series of peculiarities.

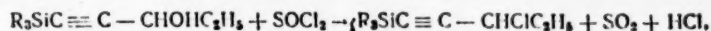
In the present work we studied the reaction of chlorosilanes with bis(bromomagnesium) derivatives of secondary acetylenic alcohols. On the basis of this reaction a method was developed for the preparation of secondary γ -silicon-containing acetylenic alcohols according to the scheme:



where R and R' are CH_3 , C_2H_5 , etc.

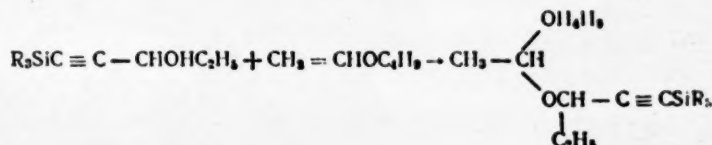
The reaction of the compounds obtained with thionyl chloride and vinyl ethers was investigated.

The reaction of secondary γ -silicon-containing alcohols with thionyl chloride showed that the replacement of the hydroxyl by a chlorine atom proceeds under comparatively mild conditions. The main reaction products were the corresponding silicoacetylenic chlorides.



where R is CH_3 and C_2H_5 . Rupture of Si-C bonds was not observed.

The reaction with vinyl ethers proceeded smoothly to form the corresponding acetals.



R = CH_3 and C_2H_5 .

5-Trimethylsilylpent-4-yn-3-ol $(\text{CH}_3)_3\text{SiC}\equiv\text{C}-\text{CHOHC}_2\text{H}_5$. To the Grignard reagent from 65.4 g (0.6 mole) of ethyl bromide and 14.58 g (0.6 g-atom) of magnesium in 200 ml of absolute ether was added 25.2 g (0.3 mole) of ethylethynylcarbinol dropwise with stirring and cooling. The mixture was then stirred for 2 hr with cooling in ice water and for 5-6 hr at room temperature. To the reaction mixture was added 0.5 g of Cu_2Cl_2 and 32.5 g (0.3 mole) of trimethylchlorosilane gradually introduced at -5° . The mixture was stirred for a further 3 hr at room temperature and 5-6 hr with heating on a water bath. At the end of the synthesis, 10% hydrochloric acid was added to the reaction mixture with cooling until the precipitate dissolved completely. The aqueous layer was separated from the ether layer, and after the usual treatment, vacuum distillation yielded 25.2 g (55%) of 5-trimethylsilylpent-4-yn-3-ol with b. p. $57.5^\circ/3$ mm, n_D^{20} 1.4452, d_4^{20} 0.8604. MR_D found 48.37, for $\text{C}_9\text{H}_{16}\text{OSi}$ calculated MR_D 48.74. Found %: Si 18.13. $\text{C}_9\text{H}_{16}\text{OSi}$. Calculated %: Si 17.97.

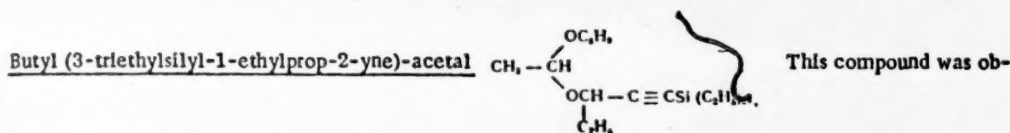
5-Triethylsilylpent-4-yn-3-ol $(\text{C}_2\text{H}_5)_3\text{SiC}\equiv\text{C}-\text{CHOHC}_2\text{H}_5$. The synthesis was analogous to that above. The reagents used were 65.4 g (0.6 mole) of ethyl bromide, 14.58 g (0.6 g-atom) of magnesium, 200 ml of absolute ether, 25.2 g (0.3 mole) of ethylethynylcarbinol, 0.5 g of Cu_2Cl_2 , and 45.2 g (0.3 mole) of triethylchlorosilane. We isolated 25.6 g (44.6%) of 5-triethylsilylpent-4-yn-3-ol with b. p. $106^\circ/7$ mm, n_D^{20} 1.4601, d_4^{20} 0.8851. MR_D found 61.37, $\text{C}_{11}\text{H}_{22}\text{OSi}$ calculated MR_D 61.38. Found %: Si 14.58. $\text{C}_{11}\text{H}_{22}\text{OSi}$. Calculated %: Si 14.2.

3-Chloro-5-trimethylsilylpent-4-yne $(\text{CH}_3)_3\text{SiC}\equiv\text{C}-\text{CHClC}_2\text{H}_5$. Into a three-necked, round-bottomed, 50-ml flask with a reflux condenser, dropping funnel, mechanical stirrer, and thermometer were placed 7.8 g (0.05 mole) of 5-trimethylsilylpent-4-yn-3-ol and 1 g of pyridine. The mixture was then cooled, 8.92 g (0.075 mole) of thionyl chloride added gradually with stirring, and stirring continued for a further 2 hr. On the following day the mixture was again stirred at room temperature for 2-3 hr and then at 60° for the removal of SO_2 . At the end of the synthesis, the mixture was treated with 15 ml of water with cooling. The organic layer was separated from the aqueous layer, dried with calcium chloride, and vacuum distilled to yield 4.52 g (60%) of 3-chloro-5-trimethylsilylpent-4-yne with b. p. $46-47^\circ/5$ mm, n_D^{20} 1.4540, d_4^{20} 0.9090. MR_D found 52.34, for $\text{C}_9\text{H}_{15}\text{SiCl}$ calculated MR_D 52.03. Found %: Si 15.65. $\text{C}_9\text{H}_{15}\text{SiCl}$. Calculated %: Si 15.89.

3-Chloro-5-triethylsilylpent-4-yne $(\text{C}_2\text{H}_5)_3\text{SiC}\equiv\text{C}-\text{CHClC}_2\text{H}_5$. The synthesis was analogous to that described above. The reagents used were 5.84 g (0.03 mole) of 5-triethylsilylpent-4-yn-3-ol, 1 g of pyridine, and 5.35 g (0.045 mole) of thionyl chloride. We obtained 4.1 g (60.6%) of 3-chloro-5-triethylsilylpent-4-yne with b. p. $96.5-98.5^\circ/8$ mm, n_D^{20} 1.4641, d_4^{20} 0.9048. MR_D found 66.10, for $\text{C}_{11}\text{H}_{21}\text{SiCl}$ calculated 65.92. Found %: Si 12.54. $\text{C}_{11}\text{H}_{21}\text{SiCl}$. Calculated %: Si 12.96.

Butyl (3-trimethylsilyl-1-ethylprop-2-yne)-acetal $\text{CH}_3-\text{CH}(\text{OC}_2\text{H}_5)_2[\text{OCHC}\equiv\text{CSi}(\text{CH}_3)_3]$. Into the ap-

paratus described above were placed 4.68 g (0.03 mole) of 5-trimethylsilylpent-4-yn-3-ol and 3 g (0.03 mole) of vinyl butyl ether. Then 1-2 drops of concentrated hydrochloric acid were added with stirring. The temperature of the reaction mixture rose sharply to 58° . The contents of the flask were stirred for 3 hr at 80° and left overnight. On the following day the reaction mixture was neutralized with baked potassium carbonate, filtered, and vacuum distilled to yield 3.2 g (41.6%) of a substance with b. p. $102-103^\circ/8$ mm, n_D^{20} 1.4368, d_4^{20} 0.8580. MR_D found 78.11, for $\text{C}_{14}\text{H}_{28}\text{O}_2\text{Si}$ calculated MR_D 78.51. Found %: Si 11.48. $\text{C}_{14}\text{H}_{28}\text{O}_2\text{Si}$. Calculated %: Si 10.95.



tained analogously. The reagents used were 5.95 g (0.03 mole) of 5-triethylsilylpent-4-yn-3-ol and 3 g (0.03 mole) of vinyl butyl ether. The mixture heated up to 53.5° . As a result of the synthesis we isolated 4.3 g (48%) of a substance with b. p. $138-139^\circ/2.5$ mm, n_D^{20} 1.4500, d_4^{20} 0.8736. MR_D found 91.81, for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$ calculated MR_D 92.40. Found %: Si 9.40. $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$. Calculated %: Si 9.57.

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DEHYDROGENATION OF FIVE- AND SIX-MEMBERED RINGS IN THE PRESENCE OF ACTIVE CHARCOAL

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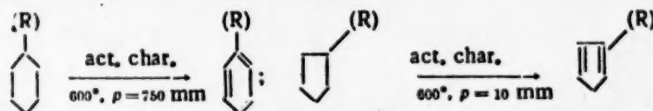
Original article submitted September 30, 1960

Activated charcoal is known to be catalytically active in different reactions, for example dehydrogenation of terpenes [1] and of cyclohexanol [2], irreversible catalysis of cyclohexane [3] and terpenes [1], isomerization of alkylcyclopropanols [4] with subsequent hydrogenation of the alkenes formed, dehalogenation of chloro-, bromo-, and iodobenzene [5], dehydrogenation of alkylidihydrogen furans [6] and others. We showed recently [7] that under the influence of different kinds of active charcoals - birch charcoal (Perm Works) with 5-6 mm particle dimensions, finely granulated "BAC" and bone charcoal - five-membered cyclenes were dehydrogenated at reduced pressures at 500-600° with the formation of the corresponding cyclopentadienes.

There is no information in the literature on the possibility of dehydrogenating five-membered rings under the influence of activated charcoal. As regards six-membered rings, Moldavskii and his co-workers [8] showed that cyclohexane at 533° and a volume rate of 0.14 hr⁻¹ gave a 17% yield of benzene, and 56.4% at 560°.

In connection with this and on the basis of our previous observations, we decided to investigate in more detail the catalytic properties of activated wood charcoal in dehydrogenation reactions of five- and six-membered rings.

We established that five- and six-membered rings undergo dehydrogenation with a high degree of conversion to the corresponding products as a result of the catalytic action of wood charcoal. Thus, at 600° and normal pressures, the amount of conversion of cyclohexane and methylcyclohexane to benzene and toluene is 97 and 100% respectively. Cyclopentane and methylcyclopentane, at the same temperature but under reduced pressure of 10-15 mm, are converted to the corresponding cyclopentadienes in respective yields of 18 and 29%:



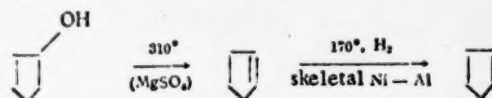
where R = H or CH₃.

It should be noted that at 600° cyclopentane and methylcyclopentane do not undergo dehydrogenation in the absence of active charcoal, and the products of the thermal conversion of cyclohexane and methylcyclohexane at this same temperature contain 6% of the corresponding aromatic hydrocarbons. A comparison of the results of thermal conversion of rings with the amount of conversion in the presence of active birch charcoal shows up the high activity of the latter for dehydrogenation of five- and six-membered rings.

EXPERIMENTAL

Original Hydrocarbons

Cyclopentane, b. p. 49.5°/754 mm, n_D^{20} 1.4070 and d_4^{20} 0.7459, was obtained by hydrogenation of cyclopentene, which in its turn was prepared from cyclopentanol by its dehydration over anhydrous magnesium sulfate at 310°:



Methylcyclopentane, b. p. 72°/759 mm, n_D^{20} 1.4100 and d_4^{20} 0.7492, was obtained by isomerization of cyclohexane (b. p. 80.8°/758 mm, n_D^{20} 1.4262, d_4^{20} 0.7787) during its continuous slow distillation over aluminum chloride through a column with an efficiency of 20 theoretical plates.

Methylcyclohexane had b. p. 101°/757 mm, n_D^{20} 1.4231 and d_4^{20} 0.7698.

The catalyst was an activated birch charcoal from the Perm Works with a specific surface area of 519 m²/g and an ash content of 0.48%.

Dehydrogenation of Five and Six-Membered Rings on Active Charcoal

Initial ring system	Pressure, mm Hg	Temp. °C	Rate of flow, hr ⁻¹	Yield of catalyzate, %	n_D^{20} of catalyzate	Catalyst of dehydrogenation products in catalyzate, %
Catalyst - birch charcoal from Perm Works						
Cyclopentane	10	550	0.1	84.0	1.4140	14
"	10	600	0.1	81.7	1.4180	18
Methylcyclopentane	10	500	0.1	90.2	1.4230	11
"	12	550	0.1	89.4	1.4245	16
"	15	600	0.1	84.1	1.4295	29
Cyclohexane	755	500	0.3	80.4	1.4723	70
"	754	500	0.1	79.9	1.4775	76
"	754	550	0.1	79.0	1.4808	82
"	756	600	0.3	76.1	1.4940	93
"	754	600	0.1	75.3	1.4977	97
Methylcyclohexane	756	500	0.1	81.2	1.4518	44
"	756	550	0.1	74.2	1.4935	95
"	756	600	0.1	74.8	1.4970	100
No catalyst						
Cyclopentane	15	600	0.1	90.9	1.4070	0
Methylcyclopentane	15	600	0.1	88.1	1.4100	0
Cyclohexane	758	550	0.1	77.9	1.4262	0
"	758	600	0.1	74.3	1.4290	6
Methylcyclohexane	750	500	0.1	81.2	1.4233	0
"	750	550	0.1	71.5	1.4242	2
"	750	600	0.1	70.1	1.4265	6

In experiments without the charcoal, the glass tube was filled with pieces of quartz. The initial hydrocarbons were fed in 10-ml portions at a rate of 0.3-0.1 hr⁻¹. Immediately after the experiments had been carried out, the amount of cyclopentadienes present in the dehydrogenation products of five-membered rings was determined colorimetrically [9]. The content of aromatic hydrocarbons in the catalyzates of cyclohexane and methylcyclohexane was found refractometrically after distillation over sodium [10].

The experimental results for the dehydrogenation of five- and six-membered rings in the presence of activated birch charcoal are given in the table. It can be seen that cyclopentane and methylcyclopentane are dehydrogenated to the corresponding cyclopentadienes; their concentrations in the catalyzate, obtained in the experiment at 600° with a rate of inflow of initial hydrocarbon of 0.1 hr⁻¹ and 10-15 mm pressure, were 18 and 29% respectively. The amount of dehydrogenation of cyclohexane and methylcyclohexane to aromatic hydrocarbons at the same temperature but at normal pressures was 97-100%; the catalyzate yields were 75.3 and 74.8%. Dehydrogenation of cyclohexane at 500° and a volume rate of 0.3 gives a catalyzate containing 70.0% benzene, and at 600° and three times the volume rate the benzene concentration in the product reaches 93%. It can also be seen from the experimental results that the temperature factor affects the yield of dehydrogenation products considerably. Thus a temperature increase from 500 to 600° increases the yield of aromatic hydrocarbons in the dehydrogenation of cyclohexane by 23-21%, and of methylcyclopentane by over 2.5 times. The rate of inflow of initial hydrocarbon is of less significance in the dehydrogenation of ring systems; a threefold decrease in the rate of inflow of cyclohexane, from 0.3 to 0.1 hr⁻¹, only increases the amount of benzene from 93 to 97%.

Gas-liquid chromatographic methods showed that the catalyzate of cyclohexane (b. p. 78-80° at 759 mm, n_D^{20} 1.4979, d_4^{20} 0.8768) obtained at 600° contained only the initial cyclohexane (about 3%) apart from benzene. Similarly, the catalyzate of methylcyclohexane (b. p. 90-110° at 752 mm, n_D^{20} 1.4970, d_4^{20} 0.8728) was found to contain up to 20% benzene together with toluene. This indicates the occurrence of a secondary reaction of demethylation of toluene to benzene under certain conditions. We shall be investigating the catalytic action of activated charcoal in more detail.

Experiments carried out in the absence of any catalyst, for comparison, showed that at 600° cyclopentane and methylcyclopentane do not undergo dehydrogenation to any marked extent. Cyclohexane at 550° also comes out of the reaction zone unchanged, but at 600° the cyclohexane condensate contains 6% benzene. The methylcyclohexane condensate was found to contain toluene at 550°, but only in small amounts - about 2%; at 600° the toluene content of the condensate was 6%.

Thus, this investigation has established that activated birch charcoal brings about the dehydrogenation of five- and six-membered rings at increased temperatures with high yields of dehydrogenation products. At 600° there are 97 and 100% conversions respectively of cyclohexane and methylcyclohexane to aromatic hydrocarbons; cyclopentane and methylcyclopentane, under the same conditions, are converted to up to 29% of the corresponding cyclopentadienes.

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SEPARATION OF NIOBIUM AND TANTALUM BY EXTRACTION OF NIOBIUM N-BENZOYLPHENYLHYDROXYLAMINATE

Corresponding Member Academy of Sciences of the USSR

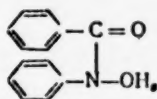
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The separation of niobium and tantalum is rightly considered one of the most difficult problems in analytical chemistry [1]. The most promising method for separating these two elements is extraction of internal complex compounds with organic solvents. It is found that a very convenient reagent for this purpose is an analog of cupferron, namely N-benzoylphenylhydroxylamine (BPHA)



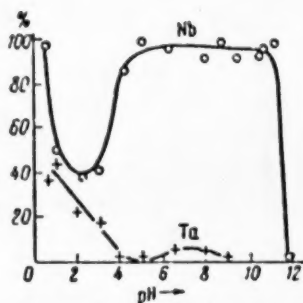
which forms a chloroform-soluble complex with niobium. This reagent was recently used for the quantitative determination of Zr, Th, and Sc [2] and also for the gravimetric determination of niobium and tantalum [3-5]. In one review on extraction [6] there was a brief report on the possibility of extracting tantalum with a solution of BPHA in chloroform in the presence of fluoride ion. It should be noted that the gravimetric method has a series of well-known drawbacks connected with the high surface of contact of phases and as a result, considerable coprecipitation, which necessitates at least two precipitations. Extraction from F⁻-containing solutions requires the use of polyethylene vessels. In one of our papers [7] it was shown that the extraction of the internal complex compound of niobium with BPHA is possible in the presence of tartaric acid, which holds the niobium and tantalum in solution but does not prevent extraction.

To follow the extraction we used radioactive isotopes of niobium and tantalum (Nb⁹⁵, T_{1/2} 35 days; Ta¹⁸², T_{1/2} 115.1 days). In order to eliminate incomplete isotopic exchange, the radioactive isotopes were added to the stable isotopes before solution of niobium and tantalum pentoxide. The solutions were prepared by dissolving samples of Nb₂O₅ and Ta₂O₅ in a mixture of conc. H₂SO₄ and (NH₄)₂SO₄ with subsequent solution of the melt in tartaric acid. Into a tube with a ground stopper was placed 4 ml of the solution and then 1 ml of a 10% alcohol solution of BPHA added. After the precipitate had formed, 5 ml of chloroform was added and the mixture shaken for 3 min. The pH of the aqueous phase remained the same after extraction in all experiments. Then 2 ml of solution was taken from the organic phase and the solution activity measured by means of a γ-counter. The results of the measurements were used to construct extraction curves for niobium and tantalum (figure).

In the pH region of 4-6, 98-100% of niobium was extracted in one operation, while the tantalum was not extracted at all. During the extraction of tantalum at pH 0.5-3.0, the tantalum compound partly floated at the interphase. This is apparently explained by the fact that tantalum forms polynuclear compounds, which are precipitated, but do not dissolve in the organic layer. In the pH region of 6-9, data on the extraction of tantalum were poorly reproducible.

Separation of Niobium from Tantalum by Extraction of Niobium
N-Benzoylphenylhydroxylamine

Taken, mg		$\frac{\text{Nb}_2\text{O}_5}{\text{Ta}_2\text{O}_5}$	Isotope	Counts/min after extraction		Extraction, %	
Nb ₂ O ₅	Ta ₂ O ₅			organic phase	aqueous phase	Nb ₂ O ₅	Ta ₂ O ₅
10,0	1,0	10:1	Nb ⁹⁵	1164	—	160,0	—
10,0	0,1	100:1	Nb ⁹⁵	1024	—	98,1	—
10,0	0,1	100:1	Ta ¹⁸²	0	1152	—	0
1,0	10,0	1:10	Nb ⁹⁵	1536	—	98,8	—
1,0	10,0	1:10	Ta ¹⁸²	—	2624	—	1,8
0,1	10,0	1:100	Nb ⁹⁵	1797	—	97,9	—
0,1	10,0	1:100	Ta ¹⁸²	32	—	—	2,5



Chloroform extraction of the compound of Nb and Ta with BPHA in relation to solution pH.

The new separation method was checked on artificial mixtures of niobium and tantalum. Standard solutions of niobium and tantalum, which were prepared as described above, were mixed before separation (pH 4.5-5.0). In each case, one of the elements contained a radioactive isotope. The results of the experimental check (see table) confirmed the possibility of successful and rapid separation of niobium and tantalum between Nb:Ta ratios of 100:1 and 1:100.

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SYNTHESIS AND CHEMISTRY OF 3-NITROPROPENE

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(Presented by Academician M. I. Kabachnik, November 1, 1960)

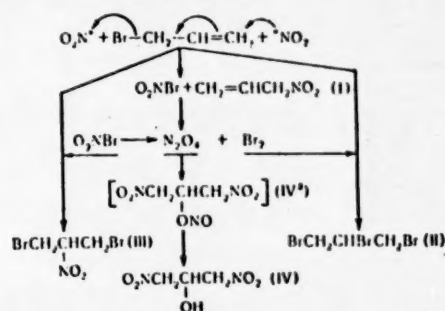
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The only convenient method for preparing 3-nitropropene, which is an interesting intermediate in the synthesis of polynitro compounds, is the exchange reaction between allyl iodide and bromide with silver nitrite (Meyer's reaction) [1, 2]. Reproduction of the reaction of acetylene with nitromethane, which forms 3-nitropropene, involves considerable difficulties [3], while the synthesis of the compound by nitration of propene with nitrogen pentoxide is complex experimentally [4].

We unexpectedly discovered that the nitration of allyl iodide and bromide with nitrogen tetroxide in ether at -20° gives a good yield of 3-nitropropene [1]. The nitryl iodide and bromide arising in this case are converted into the more stable nitrogen tetroxide and molecular iodine (liberated during the nitration of allyl iodide) and bromine. On liberation, the latter, in contrast to iodine, brominates the starting allyl bromide to give 1,2,3-tribromopropene (II). The appearance of 2-nitro-1,3-dibromopropene (III) may be explained by nitrohalogenation of allyl bromide by nitryl bromide.

When the reaction temperature was raised (in the case of allyl iodide and bromide), the reaction of the 3-nitropropene formed with nitrogen tetroxide led to 1,3-dinitropropan-2-ol (IV), which may be regarded as a secondary nitration product.

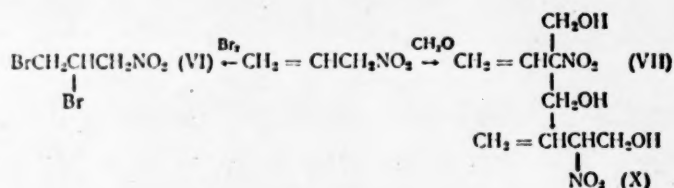


Due to the higher strength of the chlorine-carbon bond, allyl chloride did not exchange the halogen for a nitro group under analogous conditions and was not converted to 3-nitropropene, and only 1-nitro-3-chloropropan-2-ol (V) was formed.

As a result of studying the chemical conversions of 3-nitropropene, we obtained substances which confirmed the structure of some of the reaction products of allyl bromide and iodide with nitrogen tetroxide. The absence of appreciable intereffect of the double bond and the nitro group [5] indicates a combination of the properties of ethylene and nitroethane in 3-nitropropene. Therefore, its nitration with nitrogen tetroxide was

completed by the synthesis of 1,3-dinitropropan-2-ol, which was liberated as a result of the hydrolysis of the initially formed nitrite (IVa) and was identical with the product (IV); bromination gave the only possible product, 1-nitro-2,3-dibromopropane (VI), which was isomeric with (III), and consequently the latter had the structure proposed; condensation with formaldehyde led to 2-nitro-2-hydroxymethyl-3-buten-1-ol (VII), which was characterized as the diacetate (VIII) and dibromide (IX).

By elimination of the hydroxymethyl group (VII) was converted into 3-nitro-1-buten-4-ol (X), which in accordance with data of Bulgarian investigators [6], is the starting material for the synthesis of 2-nitro-1,3-butadiene.



The reaction described is the first example of the synthesis of nitro compounds by substitutive nitration of allyl halides with nitrogen tetroxide. Its mechanism apparently consists in a conjugated allyl rearrangement involving allyl iodide or bromide and nitrogen tetroxide.

I. Preparation of 3-nitropropene by nitration of allyl bromide with nitrogen tetroxide. Into a three-necked flask with ground joints, fitted with a stirrer with a glass piston seal, a calcium chloride tube, a low-temperature thermometer, and a dropping funnel with a cooling jacket, was placed 26.2 ml (36 g, 0.3 mole) of freshly distilled allyl bromide and 75 ml of dry ether. Over a period of 30 min, 18.3 ml (0.3 mole) of nitrogen tetroxide in 10 ml of ether cooled to -40° was added with vigorous stirring at a temperature no higher than -20° . After the mixture had been stirred at this temperature for 4 hr, the nitrogen oxides and ether were removed in a water-pump vacuum.

The nitration products (yield 48 g, 90% of theoretical) were washed several times with distilled water, dried over sodium sulfate, and distilled first in a water-pump vacuum and then with an oil pump;

1st fraction: b. p. $65-66^\circ$ (95 mm), 3-nitropropene (I). It had b. p. $79-80^\circ$ (180 mm), n_D^{20} 1.4270, d_4^{20} 1.056 (literature data: b. p. 80° (180 mm), n_D^{20} 1.4270, d_4^{20} 1.05). The yield was 10 g (35% of theoretical).

2nd fraction: b. p. $73-75^\circ$ (3 mm). Washing with 10% sodium carbonate solution and redistillation yielded 1,2,3-tribromopropane (II). It had b. p. 216° (754 mm), n_D^{20} 1.5840, d_4^{20} 1.4215 (literature data: b. p. $218-222^\circ$ (760 mm), n_D^{20} 1.5835, d_4^{20} 1.43).

3rd fraction: b. p. 110° (3 mm). Redistillation gave 2-nitro-1,3-dibromopropane (III). n_D^{20} 1.5392, d_4^{20} 2.10, MRD found 36.85, calculated 37.102; molecular weight found (ebullioscopically) 241, 225; calculated 246.9.

Found %: C 14.37, 14.69; H 1.91, 2.13; N 5.66, 5.94. $\text{C}_3\text{H}_5\text{O}_2\text{NBr}_2$. Calculated %: C 14.59; H 2.04; N 5.67.

II. Preparation of 3-nitropropene by nitration of allyl iodide with nitrogen tetroxide. A 16.8-g sample (0.1 mole) of allyl iodide, which had been freshly distilled in a stream of carbon dioxide, in 25-40 ml of dry ether was nitrated at -20° with 6.1 ml (0.1 mole) of nitrogen tetroxide with vigorous stirring. Two to three minutes after the first portions of nitrogen tetroxide had been added, the liberation of iodine began and the reaction mixture gradually acquired a dark brown color. After the mixture had been kept at -20° for 3 hr, the residues of nitrogen tetroxide and ether were removed in a water-pump vacuum and the iodine removed by filtration. The nitration products were washed with water, treated with metallic mercury to remove iodine, dried over sodium sulfate, and distilled.

The fraction with b. p. $78-80^\circ$ (180 mm) was 3-nitropropene (I). The yield was 35-40% of theoretical. The residue was a heavy brown liquid, which consisted of nitration products of allyl iodide.

III. Nitration of allyl chloride with nitrogen tetroxide. Over a period of an hour and at a temperature of no higher than -15° , a cooled solution of 18.3 ml (0.3 mole) of nitrogen tetroxide in 10 ml of ether was added with vigorous stirring to 24.2 ml (0.3 mole) of freshly distilled allyl chloride in 75 ml of dry ether. After the mixture had been kept at this temperature for 4 hr, the residues of nitrogen tetroxide, ether, and unreacted allyl chloride were removed in a water-pump vacuum. After being washed with distilled water and dried, the nitration products (80% of theoretical yield) were distilled at $103-105^{\circ}$ (5 mm) to yield a colorless liquid, which consisted of the product V. n_D^{20} 1.485, d_4^{20} 1.450; molecular weight: found 137, calculated 139.5.

Found %: N 10.51, 10.70. $C_3H_5O_3NCI$. Calculated %: N 10.03.

IV. 1,3-Dinitropropan-2-ol (IV). Over a period of half an hour, a cooled solution of 6.1 ml (0.1 mole) of nitrogen tetroxide in 10 ml of dry ether was added with vigorous stirring to 8.7 g (0.1 mole) of 3-nitropropene in 50 ml of dry ether at -15° . After the mixture had been stirred at -10 to -15° for 4 hr and the ether removed in a water-pump vacuum, the precipitated crystals were separated from the liquid products by filtration and washed with small portions of cooled chloroform. The 1,3-dinitropropan-2-ol (IV) had m. p. $73-74^{\circ}$ (from ethyl acetate) and was obtained in a yield of 5.2 g (35% of theoretical). Molecular weight: found by Rast's method 135, 142; calculated 150.

Found %: C 24.79, 24.84; H 4.32, 4.11; N 18.80, 18.66. $C_3H_5O_5N_2$. Calculated %: C 24.0; H 4.00; N 18.66.

V. 1-Nitro-2,3-dibromopropane (VI). A solution of 8.3 ml (0.1 mole) of 3-nitropropene in 25 ml of dry chloroform was brominated with 5.1 ml of bromine (0.2 mole) with stirring and cooling to 10° . After the reaction mixture had been decolorized, the chloroform was removed and the 1-nitro-2,3-dibromopropane distilled at 115° (3 mm). The yield was 23 g (94% of theoretical). n_D^{20} 1.5451, d_4^{20} 2.10; MR_D calculated 37.102, found 37.34.

Found %: C 14.84, 14.74; H 1.89, 2.09; N 5.85, 5.90. $C_3H_5O_2NBr_2$. Calculated %: C 14.57; H 2.04; N 5.67.

VI. 2-Nitro-2-hydroxymethyl-3-buten-1-ol (VII). To mixture of 8.7 g (0.1 mole) of freshly distilled 3-nitropropene and 16.5 g (0.22 mole) of 40% formalin solution was added 50 mg of potassium carbonate with stirring. After 20 min, the temperature rose rapidly to 70° due to the heat of reaction. After the temperature had fallen to 35° , the reaction mixture was stirred for a further 6 hr. The reaction product was isolated by two extractions with ether; the ether extracts were washed several times with saturated sodium chloride solution and dried over baked sodium sulfate. The residue was an oily liquid which crystallized after standing for two days in a vacuum desiccator. The 2-nitro-2-hydroxymethyl-3-buten-1-ol formed colorless crystals with m. p. 45° (from chloroform) and the yield was 12.5 g (80% of theoretical).

Found %: N 9.41, 9.45. $C_5H_9O_4N_2$. Calculated %: N 9.50.

VII. Acetate of 2-nitro-2-acetoxymethyl-3-buten-1-ol (VIII). A mixture of 1.47 g (0.01 mole) of 2-nitro-2-hydroxymethyl-3-buten-1-ol and 2.6 g (0.025 mole) of acetic anhydride was heated for 4 hr and the reaction mixture poured into water, washed several times with dilute potassium carbonate solution and water, and extracted with ether, and the ether solution washed with water and dried with sodium sulfate. The diacetate was a light yellow liquid with n_D^{20} 1.4610.

Found %: N 6.43, 6.35. $C_9H_{13}O_6N$. Calculated %: N 6.06.

VIII. 2-Nitro-3,4-dibromo-2-hydroxymethylbutan-1-ol (IX). A solution of 0.875 g of 2-nitro-2-hydroxymethyl-3-buten-1-ol and 0.8 g of bromine in 20 ml of dry chloroform was stirred and irradiated with an infrared lamp, and the color disappeared after 5 hr. The thick mass remaining after removal of the chloroform and treatment with benzene was recrystallized from dichloroethane, when it had m. p. 92° .

Found %: C 20.39, 19.38; H 2.68, 2.61; Br 51.34, 52.27. $C_6H_9Br_2O_2N$. Calculated %: C 20.49; H 3.09; Br 54.54.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

DIPOLE MOMENTS OF ORGANOTIN CHLORIDES AND THEIR COMPLEX-FORMING POWER

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The physicochemical properties of organotin chlorides have not been studied adequately. In particular, one of the most important parameters characterizing the nature of chemical bonds, namely the dipole moment, has been determined only for three compounds of this class: $(C_2H_5)_2SnCl_2$ 3.85 D [1], $(C_2H_5)_3SnCl$ 3.44 D [1] and $(C_6H_5)_3SnCl$ 3.28 D [2]. Therefore, it is important to obtain new data on the polar properties of these compounds. A very interesting and important property of stannic chloride is its capacity to form molecular compounds of various stabilities with a series of substances. This property apparently determines its catalytic activity in polymerization. It seemed interesting to determine the change in the complex-forming power when the chlorine atoms in $SnCl_4$ were replaced by organic radicals.

In accordance with this, the present work consisted of two parts, namely the determination of the dipole moments of organotin chlorides and the investigation of their complex-forming power by the method of dielectric polarization. The dipole moments μ of the compounds studied were measured in hexane, benzene, and dioxane and are given in Table 1.

TABLE 1

Compound	μ			$\mu_b - \mu_h$	$\mu_d - \mu_h$
	hex- and	ben- zene	di- oxane		
$SnCl_4$	0 (10)	0.87	3.82(10)	0.87	3.82
$C_6H_5SnCl_3$	3.99	4.24	5.81	0.25	1.82
$(C_6H_5)_2SnCl_2$	3.65	3.59	4.34	-0.06	0.69
$(C_6H_5)_3SnCl$	(3.30)	3.31	3.93	—	0.63
$(n-C_4H_9)_2SnCl_2$	4.25	4.22	5.11	-0.03	0.85
$(n-C_4H_9)_3SnCl$	3.58	3.64	4.03	0.06	0.45

According to electron-diffraction data [3, 4], the stannic chloride molecule has a tetrahedral configuration; consequently, its dipole moment in the vapor state and in indifferent solvents should equal zero. This has been confirmed experimentally for $SnCl_4$ in the vapor state [5], in hexane [1], and in the solid state [6]. However, the dipole moment of $SnCl_4$ in benzene is not zero and equals 0.8 D according to data in [6] and 0.96 D according to data in [7]. The existence of a dipole moment for $SnCl_4$ in benzene and also in carbon tetrachloride was the reason why a pyramidal configuration was proposed for $SnCl_4$ [7]. We repeated the measurement of

the dipole moment of SnCl_4 in benzene, taking special precautions to prevent the entry of moisture, and obtained a value of 0.87 D. This value agrees well with the data presented above.

In our opinion the dipole moment of SnCl_4 in benzene is not due to a pyramidal configuration of the molecule as was stated in [7], but the formation of a molecular compound of stannic chloride and benzene.

We are studying the polar properties of molecular compounds of stannic chloride and other metal halides with unsaturated hydrocarbons; the results will be published later. In an examination of the dipole moments of chloroorganic compounds of tin it is very important to know whether the tetrahedral configuration of the bonds is retained in these compounds or whether there is distortion of the tetrahedra as a result of a form of hybridization or steric hindrance. According to structural analysis data, the compounds $\text{Sn}(\text{CH}_3)_4$, $(\text{CH}_3)_3\text{SnI}$, $(\text{CH}_3)_3\text{SnCl}$, $(\text{CH}_3)_2\text{SnCl}_2$ have a tetrahedral configuration [8]. Apparently, the tetrahedral direction of the bonds is also retained in the compounds we studied. If this is so, the dipole moments of $\text{C}_6\text{H}_5\text{SnCl}_3$ and $(\text{C}_6\text{H}_5)_3\text{SnCl}$ in hexane should be similar. The difference of 0.7 D (Table 1) indicates considerable interaction of the π -electrons of the phenyl rings with the electrons of the $\text{Sn}-\text{Cl}$ bonds.

The dipole moments of organotin chlorides with aliphatic radicals are higher than those of the corresponding compounds with phenyl radicals. If it is assumed that the dipole moment of the $\text{Sn}-\text{Cl}$ bond is the same in all compounds and equals 3.0 D [9], the dipole moment of the $\text{Sn}-\text{C}$ bond in aliphatic compounds equals 0.58 D according to data for $(\text{C}_4\text{H}_9)_3\text{SnCl}$ and 0.63 D according to data for $(\text{C}_4\text{H}_9)_2\text{SnCl}_2$, i.e., they are practically the same and equal 0.6 D.

This constancy is not observed in phenyl derivatives; the moment of the $\text{Sn}-\text{C}$ bond equals 1 D, 0.2 D, and 0.3 D in mono-, di-, and triphenyl derivatives, respectively. In contrast to aliphatic compounds, these compounds show a deviation from additivity due to the intereffect of the phenyl radicals and the chlorine atoms.

The dipole moment of stannic chloride in dioxane equals 3.82 D [10]. The high dipole moment indicates the formation of a complex of the donor-acceptor type. The dipole moments of organotin chlorides in dioxane are also higher (Table 1) than in benzene and hexane. Since the compounds studied do not contain hydrogen atoms which are capable of giving hydrogen bonds, the dipole moment here cannot be high due to the normal dioxane effect. The increase in the moment in dioxane is explained by interactions of the donor-acceptor type.

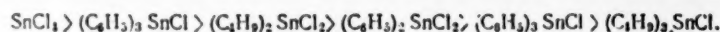
TABLE 2

Measurements in Benzene Containing Phenyltin Trichloride (0.0744 mole/liter)

Compound	P_{∞}	R_D	μ_{exp}	μ in benzene
$n\text{-C}_4\text{H}_9\text{SH}$	73.0	28.4	1.47	1.48
$(n\text{-C}_4\text{H}_9)_2\text{S}$	109.4	47.2	1.73	1.57
CH_3OH	229.6	8.3	3.27	1.67
$\text{C}_2\text{H}_5\text{OH}$	247.3	13.0	3.37	1.67
$\text{C}_4\text{H}_9\text{O}$	234.2	20.1	3.22	1.71

Table 1 gives the differences in dipole moments of the compounds studied in dioxane and hexane. To a certain extent, these values may characterize the complex-forming power of the tin compounds studied with dioxane. As can be seen, it differs for different compounds and falls sharply when the chlorine atoms are replaced by organic radicals.

The compounds may be arranged in the following series with respect to complex-forming power:



Among the organotin compounds studied, phenyltin trichloride was investigated in most detail. We studied the complex-forming power of this compound with other substances in more detail by means of dielectrometric titration.

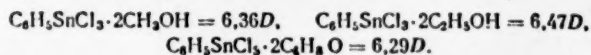
Table 2 gives the dipole moments of a series of compounds in benzene containing phenyltin trichloride (0.0744 mole/liter).

As can be seen, the dipole moments of butyl mercaptan and dibutyl sulfide in the presence of phenyltin trichloride were close to the dipole moments in benzene. In addition, in these systems there was a linear relation between ϵ (the dielectric constant) and C of the donor over a wide range of concentrations. Consequently, these compounds do not give complexes of the donor-acceptor type with phenyltin trichloride.

The relation between ϵ and C was quite different when methanol, ethanol, and tetrahydrofuran were added to the solution. In all the systems there was first a sharp increase in the dielectric permeability of the solutions up to a ratio of the phenyltin trichloride and donor concentrations of 1:2, and then the course of the curve changed. The dipole moments of the compounds found by extrapolation from experimental data on the first part of the curve were almost twice the dipole moments of the corresponding compounds in benzene (Table 2). These facts indicate the formation of complexes of the donor-acceptor type in the systems studied.

From analysis of the data on ϵ and C it is possible to conclude that complex formation here is not complete with the addition of two donor molecules, and there is further interaction of the complex with the added substance.

The dipole moments found by extrapolation from the experimental data referring to the first part of the ($\epsilon - C$) curve are as follows:



If the catalytic activity of stannic chloride in polymerizations is connected in some way with its power to give corresponding complexes, then on the basis of results obtained one would expect that some organotin chlorides would be active in this way. Among the compounds studied, this applies above all to phenyltin trichloride. It is possible that the sequence of changes in the catalytic activity of the tin compounds studied in the present work will be the same as given above for complex formation.

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NEW SYNTHESIS OF 19-NOR-11-DESOXYCORTICOSTERONE ACETATE

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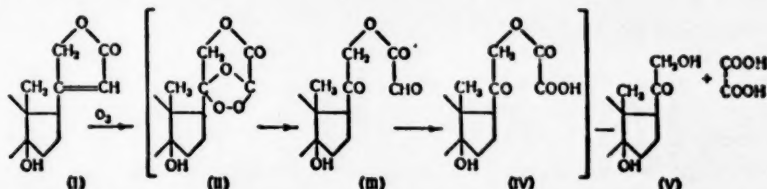
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19-Nor-11-desoxycorticosterone acetate was first synthesized by Ehrenstein [1] from strophanthidin, but it was an amorphous product which evidently consisted of stereoisomers and did not have biological activity. Another group of investigators [2, 3] later synthesized 19-nor-11-desoxycorticosterone acetate from 19-nor-17-ethynyltestosterone. The substance obtained was found to be twice as active as the natural hormone. Starting from strophanthidin Barber and Ehrenstein [4] also synthesized 19-nor-11-desoxy-10 α -14 β ,17 α -corticosterone. As is characteristic of all corticosteroids of the 17-iso series with cis-coupling of rings C and D, the compounds synthesized did not have an appreciable mineralocorticoid action.

Starting from strophanthidin, we achieved a new synthesis of 19-nor-11-desoxycorticosterone acetate with a configuration corresponding to natural 11-desoxycorticosterone.

The lactone ring of strophanthidin was converted into an α -ketol chain by ozonization. With cardiac aglycones this reaction is normally [5, 6] effected in three stages. The ozonide formed in the first stage is reduced with zinc dust in acetic acid to a glyoxalic ester. The latter is hydrolyzed by potassium bicarbonate in aqueous methanol to the ketol. In this case the side chain at C₁₇ retains its β -orientation, though there are data [7] indicating that there is a possibility of its isomerization during alkaline hydrolysis. Isomerization does not occur under mild acid hydrolysis (see [8]).

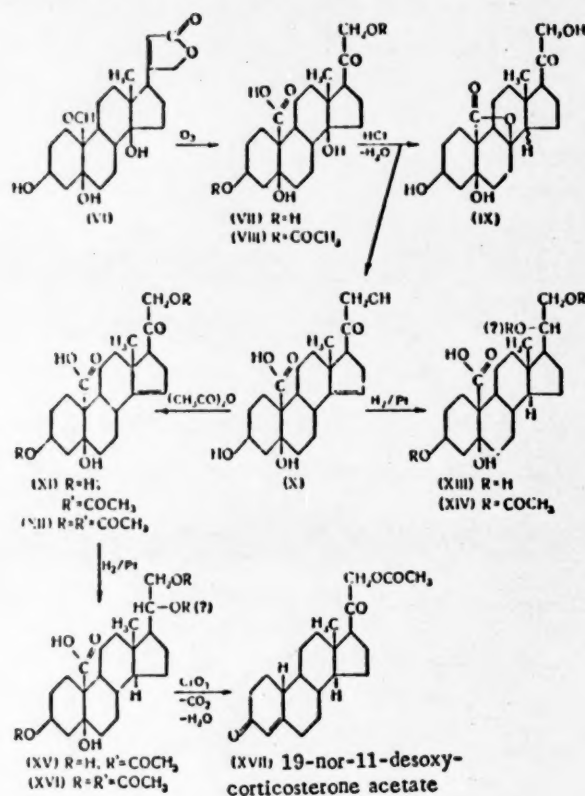
In our experiments the lactone ring (I) was converted into the α -ketol side chain (V) in one stage. A solution of strophanthidin (VI) in acetone was ozonized at -72° until a blue color appeared. The acetone was evaporated at room temperature, the residue dissolved in aqueous ethanol, and the solution left to evaporate slowly at 36-37° for 2-3 days. The following reactions apparently occurred successively in this case: decomposition of the ozonide (II) with the formation of the glyoxalic ester (III), oxidation of the aldehyde group of the glyoxalic acid to a carboxyl group, and spontaneous hydrolysis of the acid ester of oxalic acid (IV) formed to the ketol (V). That the process occurred in precisely this way was confirmed by the fact that oxalic acid was found in the mother solution after separation of the ketol and identified as the anilide.



At the same time, either during ozonization (strophanthidin is readily oxidized to strophanthidinic acid even in air) or during oxidation of the aldehyde group of the glyoxalic acid, the aldehyde group at C₁₉ was

oxidized to a carboxyl group so that the final product of ozonolization was 3 β ,5,14,21-tetrahydroxy-20-OH-14-isopregnane-19-carboxylic acid C₂₁H₃₄O₇ (VII) with m. p. 216-217° and $[\alpha]^{21}_D = +64.8^\circ \pm 1^\circ$ (C = 2.59% in methanol). The yield was 68-70%.

The action of acetic anhydride in pyridine on the tetrahydroxyketo acid (VII) obtained gave the diacetate (VIII) with m. p. 208-209° and $[\alpha]^{22}_D = +40.2^\circ \pm 0.5^\circ$ (C = 1.66% in methanol).



In the second stage of the synthesis, dehydration of the hydroxyl group at C₁₄, which was effected by heating substance (VII) with a 1% solution of hydrogen chloride in methanol, led to an amorphous product (X). At the same time, there was the formation of a small amount (1-1.5%) of another neutral product C₂₁H₃₀O₆ (IX) with m. p. 265-268° and $[\alpha]^{25}_D = +164.5^\circ \pm 2.5^\circ$ (C = 1.48% in pyridine), which was apparently the 19,8-lactone of 3 β ,5,8,21-tetrahydroxy-20-OH-14-pregnane-19-carboxylic acid and had a structure analogous to the lactone of strophanthidinic acid [9] and also the lactone obtained under similar conditions during the dehydration of 3 β ,5,14-trihydroxy-21-nor-14 β ,17 α -pregnane-19,20-dicarboxylic acid [4, 10].

The trihydroxyketo acid (X) was acetylated in two ways: with an equimolecular amount (more accurately 1.25 mole) of acetic anhydride and with excess acetic anhydride. In both cases the acetylation products were amorphous. In analysis by partition chromatography (system: chloroform-formamide; developer: alkaline solution of 3,5-dinitrobenzoic acid), the substance obtained by exhaustive acetylation was less polar and gave on a paper chromatogram a spot lying closer to the front ($R_f = 0.88 \pm 0.03$) than the product of incomplete acetylation ($R_f = 0.69 \pm 0.02$). Consequently, the substance obtained with excess acetic anhydride was the diacetyl derivative and corresponded to the formula of (XII). The other acetyl derivative must have been the monoacetate, and since the primary hydroxyl at C₂₁ is acetylated first during selective acetylation [5], it was assigned the structure (XI).

Hydrogenation of the trihydroxyketo acid (X) in acetic acid over platinum yielded a crystalline compound (XIII) C₂₁H₃₄O₆ with m. p. 235-237° and $[\alpha]^{18}_D = 50.0^\circ \pm 1.5^\circ$ (C = 1.40% in methanol). Under analogous

conditions, the monoacetyl derivative (XI) gave a crystalline substance $C_{23}H_{36}O_7$ (XV) with m. p. 198-200° and $[\alpha]^{28}_D = +129.1^\circ \pm 2^\circ$ ($C = 1.27\%$ in methanol). The yield calculated on the tetrahydroxyketo acid (VII) was 12%. During the hydrogenation, about 2 moles of hydrogen was consumed in each case. This indicates that together with reduction of the double bond at C_{14} and C_{15} , there was also reduction of the ketone group at C_{20} . Since Plattner, Ruzicka, et al. [11] have shown that hydrogenation of $\Delta^{14,15}$ -steroids with a β -configuration at C_{17} leads to a trans-configuration of rings C and D, it must be assumed that in the given case there was a similar conversion.

With excess acetic anhydride, the tetrahydroxy acid (XIII) gave a triacetate $C_{27}H_{40}O_9$ (XIV) with m. p. 171-172° and $[\alpha]^{18}_D = +60.9^\circ \pm 2.5^\circ$ ($C = 1.51\%$ in methanol). Acetylation of compound (XV) also gave a triacetate $C_{27}H_{40}O_9$ (XVI) with m. p. 209-210° and $[\alpha]^{28}_D = 106.9^\circ \pm 2.5^\circ$ ($C = 1.44\%$ in methanol). It is strange that the constants of the triacetate (XIV) do not coincide with those of the triacetate (XVI). This is evidently because the hydroxy compounds are epimeric at C_{20} . It is difficult to decide on their structures. On the basis of the difference in the molecular rotations of the hydroxysteroids themselves and their acetyl derivatives [7, 12, 13] it is only possible to surmise that the triacetate (XIV) has a β -configuration and compound (XVI) an α -configuration at C_{20} .

The final conversion of 19-nor-11-desoxycorticosterone acetate (VII) included oxidation of the secondary hydroxyl groups at C_3 and C_{20} to keto groups, dehydration of the tertiary hydroxyl groups at C_5 , and elimination of the carboxyl group at C_{10} . In practice this was achieved in one stage by oxidation of compound (XV) with chromium trioxide and by heating the crude oxidation product in glacial acetic acid. The yield, calculated on compound (XV), was 68%. Decarboxylation proceeded readily in this stage. In syntheses with strophanthidin, this is usually achieved by heating substance in high vacuum [1] or by treatment with Girard's reagent [4, 14]. It is impossible to give a satisfactory explanation for the mechanism of decarboxylation in this case. It can merely be noted that the elimination of carbon dioxide occurs only after introduction into the molecule of an α, β -unsaturated keto group, which polarizes the carbon-carbon bond between C_{10} and C_{19} . Therefore, there is the possibility that we have here one form of oxidative hydrolytic conversion [15].

The 19-nor-11-desoxycorticosterone acetate $C_{22}H_{30}O_4$ we synthesized was a crystalline substance with m. p. 172-173° and $[\alpha]^{27}_D = +144.7^\circ \pm 1.5^\circ$ ($C = 1.19\%$ in chloroform). The infrared spectrum showed the following main frequencies: 1622, 1667, 1728 cm^{-1} . There was no absorption in the region of hydroxyl groups. According to literature data, 19-nor-11-desoxycorticosterone acetate synthesized from 19-norandrostenedione [2, 3] has m. p. 173-174° and $[\alpha]_D = +150^\circ$ (in chloroform).

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RELATION OF THE CATALYTIC PROPERTIES OF METALS
TO THE DEGREE OF APPROACH OF THE STATE OF
THEIR SURFACE TO EQUILIBRIUM

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(Presented by Academician A. A. Balandin, September 17, 1960)

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Metal catalysts differ from all others in the simplicity of their chemical composition, and this facilitates the thermodynamic analysis of the conditions of equilibrium of active centers with the crystal lattice of the catalyst. A study of the kinetics of allylbenzene isomerization on platinum films [1] and also on platinum, palladium, and tungsten wires [2] showed that their catalytic activity is retained at temperatures which exceed not only the temperature at which mobility of the surface metal atoms appears ($T \approx 0.3 T_{\text{melt}}$), but also the temperature where appreciable growth of crystals begins T_G , which is known (see for example [3]) to be close to $0.4 T_{\text{melt}}$ for metals. On the basis of these data and the sudden increase in the experimental activation energy at temperatures of $0.36-0.38 T_{\text{melt}}$, a hypothesis was put forward [1, 2] that with sufficient mobility of the surface atoms, equilibrium is established between the catalyst lattice and the active centers.

In actual fact, if this equilibrium exists, the concentration of active centers will depend exponentially on their heat of formation, which is included in the experimental activation energy, increasing it sharply in comparison with the value found at lower temperatures, which refers only to the catalytic reaction.

O. M. Poltorak [4, 5] analyzed the conditions of the equilibrium nonequilibrium lattice \rightleftharpoons active centers, characterizing the degree of departure from the equilibrium of the crystals, which depends on their dispersion (or the period of the mosaic structure) and the presence in the actual crystals of forms other than those of equilibrium crystals, by the value $\Delta \lambda_r = \lambda_\infty - \lambda_r$, where λ_∞ is the heat of sublimation of coarse, right-faced crystals and λ_r is the mean energy of abstraction (per mole) of atoms from the surface of the faces of a crystal of a given type. On the basis of these ideas he examined various forms of relation of the number of active centers to the catalyst firing temperature. However, in any case at temperatures above T_G , $\Delta \lambda_r \rightarrow 0$ and the concentration of active centers must tend to an extremely low value, which follows from the theory of defects for ideal crystals.

The experimental data presented above on the existence of catalytic activity at temperatures above T_G cannot be explained by the fact that $\Delta \lambda_r$ differed substantially from zero as the catalysts were subjected to too drastic thermal treatment. To explain these results, the hypothesis was put forward [2] that the active centers in equilibrium with the catalyst lattice have two translational degrees of freedom. As is known, in some cases absorbed atoms and molecules may be regarded as a two-dimensional gas with the entropy of two-dimensional translational movement. However, in work on the theory of evaporation of metal crystals (for example [6]), the entropy of translational motion is neglected. O. M. Poltorak [4] also ignored the entropy of translational motion of atoms along the crystal surface. By allowing for this value it is possible to explain the existence of catalytic activity at high temperatures. The preexponents of the rate constants of allylbenzene isomerization on platinum films and also on platinum and palladium wires calculated on the basis of this hypothesis agree satisfactorily with experimental values [2].

If a study of the kinetics of a catalytic reaction over a sufficiently wide temperature range makes it possible to estimate the degree of approach to equilibrium of the active centers with the catalyst lattice, then this method may be used for explaining the effect of temperature and preliminary thermal treatment conditions on the catalytic properties of a metal. In particular, with temperatures at which the equilibrium concentration of active centers is not reached, the degree of approach to this should depend to a large extent on the rate of cooling of the catalyst after it has been kept at a higher temperature. After rapid cooling of the catalyst, the concentration of active centers will differ more from the equilibrium value than after slow cooling.

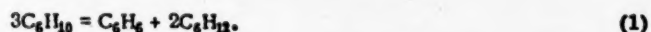
In the case of the catalytic activity of atomic structures of different numbers of atoms, the rates at which their equilibrium concentrations are established will differ. The activation energy for the establishment of equilibrium will apparently increase from simple to complex centers. Therefore, under otherwise equal conditions, with a rise in temperature the equilibrium concentrations of the simple centers will be reached first and then those of the more complex centers. A change in the ratio of the concentrations of different active centers leads to a change in the selectivity of a catalyst.

The expected effects were observed in a study of the conversions of cyclohexene on a platinum film. When the platinum film was heated to no higher than 500°, dehydrogenation of cyclohexene to benzene was observed. At temperatures of 290–485°, the experimental activation energy of this reaction equalled 23.7 ± 0.5 kcal/mole. After the film had been heated in high vacuum at 700°, the conversion of cyclohexene on it began at an appreciable rate only at temperatures above 450°, and 1,3-cyclohexadiene was formed. According to the ideas given above, this indicates that the active centers on which the dehydrogenation to benzene occurs are more complex and thermodynamically less stable at temperatures up to 700° than the centers responsible for the formation of cyclohexadiene from cyclohexene. The retention of these more complex centers at 500° indicates the high activation energy of their destruction.

For two series of experiments with a rise in temperature to 600°, the experimental activation energy of cyclohexadiene formation at 520–600° was the same and equalled 60 kcal/mole. At lower temperatures the activity of the catalyst fell, and in a third series of experiments the experimental activation energy was 60 kcal/mole over the whole temperature range from 450 to 600°. This indicates that the equilibrium concentration of active centers was established, as is confirmed by agreement of the results obtained at 544° before and after the experiment at 600° in the third series. When the activity of the catalyst at 544° was determined by nonequilibrium centers, it fell and approached the level which was found in the third series of experiments.

After "quenching" of the film (cooling from 700 to 460° in 4 min), the activation energy of cyclohexadiene formation at temperatures below 530° fell to 26 kcal/mole and the activity of the film increased sharply, while in the region of higher temperatures these parameters remained as before. It should be noted that the difference in the experimental activation energies $60 - 26 = 34$ kcal/mole was the same as for the isomerization of allylbenzene on a platinum film [1]. This indicates that the two reactions occur on equilibrium active centers of one type. If the nonequilibrium active centers which appear after quenching or during the synthesis of the catalyst have the same nature as those in equilibrium with the catalyst lattice, then the heat of formation of the latter may be determined with formula (8) in [2] from the difference in the experimental activation energies on equilibrium and nonequilibrium active centers.

A special investigation is needed to determine the mechanism of formation of either benzene or cyclohexadiene from cyclohexene in relation to the conditions of preparation and thermal treatment of the metal catalyst. That such a relation exists is indicated by the data presented above and also a comparison of them with the results of experiments on palladium and platinum films which were heated to no higher than 200°. Thus, cyclohexene is not dehydrogenated on palladium films [7] at temperatures of from 50 to 150° but is converted according to the following equation:



This is in complete agreement with the results obtained by N. D. Zelinskii and G. S. Pavlov [8] with an active palladium catalyst, on which dehydrogenation was observed at higher temperatures. The degree of conversion of cyclohexene according to the equation



increased from 1% at 164° to 89% at 320°. No unsaturated hydrocarbons were found in the catalyzates, and therefore the sum of the percentage conversions of cyclohexene according to Eqs. (1) and (2) should be close to 100 at the given temperature. This was confirmed by comparing the percentage conversions according to reaction (1) calculated from the refractive indices of the catalyzates given in [8] with the percentage of dehydrogenation given in the same article. An analogous result was obtained by B. V. Erofeev and N. V. Nikiforova [9] in studying the conversion of cyclohexene on copper catalysts; with a rise in temperature from 249 to 350°, the percentage conversion according to Eq. (1) fell, while the percentage of dehydrogenation increased. Assuming that process (1) occurs on triplets and process (2) on doublets in accordance with the multiplet theory of A. A. Balandin [10], the authors explain these results by a decrease in the number of triplets in comparison with the number of doublets with a rise in temperature. Considering data [11] on the considerable mobility of atoms on a copper surface at the temperatures of the catalytic experiments, B. V. Erofeev and N. V. Nikiforova [9] regarded the multiplets as unstable atomic aggregates, whose number could be determined by the conditions of equilibrium between multiplets and the crystal.

However, the opposite temperature dependence of the percentage conversions of cyclohexene according to Eqs. (1) and (2) was observed by N. D. Zelinskii and G. S. Pavlov [8] at much lower temperatures than those at which mobility of palladium atoms on the surface of its crystals appears. The change in the ratio of the rates of reactions (1) and (2) with a rise in temperature which was found in [8, 9] may be caused by a difference in their activation energy. The degree of retardation of these reactions by the absorption of conversion products may also be different. Therefore, the explanation given by B. V. Erofeev and N. V. Nikiforova [8] is not the only possible one.

The hypothesis used in [9] that at the temperature of 249-350° ($0.39-0.46 T_{\text{melt}}$ of copper) the crystals of copper catalysts are in equilibrium with active centers agrees with data presented above, which show that the equilibrium concentration of active centers leading to reaction (2) is established at temperatures above $0.38 T_{\text{melt}}$ of platinum. Equilibrium between the active centers for allylbenzene isomerization and the platinum film (1) was established within the range $0.36-0.38 T_{\text{melt}}$. This rule may apply to other metals.

The present article shows that a study of the kinetics of catalytic reactions over a wide temperature range makes it possible to estimate the degree of approach to the equilibrium of active centers with the catalyst lattice, and on the basis of this it is possible to explain the effect of thermal treatment on the activity and selectivity of a catalyst.

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INFRARED SPECTRA AND STRUCTURE OF SOME NONBENZENOID AROMATIC COMPOUNDS

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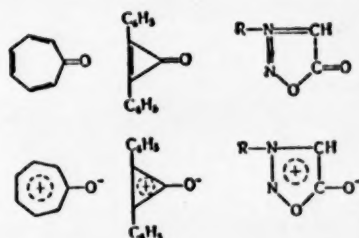
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February, 1961

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Aromatic nonbenzenoid compounds include, in particular, such carbonyl-containing compounds as tropone, diphenylcyclopropenone, and sydnones. It is assumed that the oxygen atom in such compounds attracts an electron of the ring to a considerable extent and $6-\pi$ or $2-\pi$ electrons remain in the field of the ring nuclei in accordance with Hückel's $(4n + 2)$ rule [1].



As a result of this, the $C=O$ bond in such compounds should be polarized to an appreciable extent. This polarization of the bond should have an effect on the position and intensity of the carbonyl group bands in the infrared spectra. The investigation of the position and intensity of the carbonyl band therefore may be used for characterizing the degree of aromaticity of these compounds, though it is always necessary to remember that the intensity of the $C=O$ band may be affected by other factors.

We found the positions and intensities of the carbonyl bands in the three compounds (tropone, diphenylcyclopropenone, and 3-ethylsydnone) in the liquid and crystalline states and in various solvents (see figure and table).

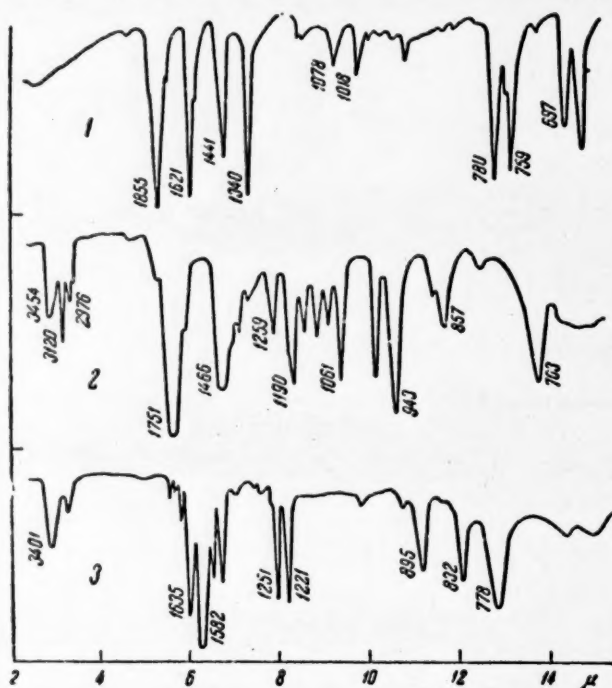
The comparatively high values of the $C=O$ frequencies found for the compounds studied (tropone 1635 cm^{-1} , 3-ethylsydnone 1751 cm^{-1} , and diphenylcyclopropenone 1855 cm^{-1}) and a comparison with the frequencies of the $C=O$ group in some other compounds (benzophenone, γ -lactone, azlactone, etc.) [2] give no grounds for considering that there is strong polarization of the $C=O$ bonds in the compounds studied. However, since the compounds used for comparison are not exact analogs of those studied, the position and displacement of the $C=O$ frequency should not be regarded as unequivocally characterizing the degree of polarity of the bond. The integral intensities of the $C=O$ group bands of the compounds studied should be more suitable for this purpose, as the intensity of the characteristic absorption in the infrared region is known to be greater, the greater the polarity of the corresponding bond in the general case.

The integral intensity of the $C=O$ bands of diphenylcyclopropenone and 3-ethylsydnone equal: 5-8 units, i.e., 4-5 times greater than in normal ketones (~ 2) [4] and twice as great as in amides [5]. The increase in

Intensity of the C=O Band of Some Nonbenzenoid Aromatic Compounds*

Compound	Intensity, mole ⁻¹ · liter · cm ⁻² · 10 ⁴		
	CCl ₄	dioxane	CH ₃ CN
Diphenylcyclopropanone	7.4	5.0	4.9
3-Ethylsydnone	7.9	6.3	6.6
Tropone 1635 cm ⁻¹	0.95	0.93	0.89
Tropone 1585 cm ⁻¹	2.6	2.7	3.2

* The intensities were measured by Burgen's method [3]; the spectra were recorded with an IKS-14 instrument.



Infrared spectra: 1) diphenylcyclopropanone (crystalline); 2) 3-ethylsydnone (liquid); 3) tropone (liquid).

Intensity of the carbonyl group in diphenylcyclopropanone and 3-ethylsydnone in comparison with normal ketones and amides indicates high polarization of the C=O group in the compounds studied and to some extent confirms the aromaticity of these compounds. In contrast to the data on the two compounds named, the integral intensity of the C=O band of tropone (to which the band at 1635-1638 cm⁻¹ is normally assigned) is found to be very low (~1.0).

The result obtained is difficult to explain, as a number of properties of tropone indicate that this compound has a certain aromaticity.

In our opinion the explanation of the observed anomaly is as follows. Adjacent to the band at 1635 cm⁻¹ in the infrared spectrum of tropone is an extremely intense band at 1585 cm⁻¹, which is usually ascribed to vibrations of the double bonds of the ring. We consider that in actual fact this band is completely or partially associated with vibrations of the carbonyl group. It should be stated that analogous splitting of the C=O group band

is also observed in the spectra of sydnone (in solutions), and the intensities we give are the sum of the intensities of the two bands. If we consider the total intensities of the bands at 1635 and 1585 cm^{-1} in tropone, the intensity obtained is of the order of 4 units, i.e., considerably greater than for simple ketones and approaching the values we found for diphenylcyclopropenone and sydnone. We also studied diphenylcyclopropenone hydrobromide. The carbonyl band at 1855 cm^{-1} was absent from the spectrum of this salt, and there appeared a broad, intense band at 2976 cm^{-1} , which was caused by the presence of the hydroxyl group in the molecule. These data agree with the structure proposed previously for the salt [6].

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SOLUBILITY ISOTHERMS AT 0° IN THE TERNARY SYSTEMS

$\text{NaBH}_4\text{--NaCl--H}_2\text{O}$ AND $\text{NaBH}_4\text{--NaBr--H}_2\text{O}$

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The solubility isotherms of the ternary system $\text{NaBH}_4\text{--NaOH--H}_2\text{O}$, which forms the basis of all water-salt systems involving sodium borohydride, are characterized by crystallization of pure sodium borohydride dihydrate, anhydrous sodium borohydride, and sodium hydroxide monohydrate [1, 2]. In the present work we studied solubility at 0°C in the ternary systems $\text{NaBH}_4\text{--NaCl--H}_2\text{O}$ and $\text{NaBH}_4\text{--NaBr--H}_2\text{O}$.

The study of these systems is of interest for establishing the conditions and form of separation of sodium borohydride from aqueous solutions containing sodium halides, the possibility of preparing new solid phases containing sodium borohydride, and further characterization of the physicochemical properties of sodium borohydride and the borohydride ion.

To prevent hydrolysis of the sodium borohydride, the solubility was studied in 1% aqueous NaOH solution, i.e., essentially we studied isoconcentrates with 1% NaOH in the quaternary systems: $\text{NaBH}_4\text{--NaCl--NaOH--H}_2\text{O}$ and $\text{NaBH}_4\text{--NaBr--NaOH--H}_2\text{O}$, which practically coincided, however, with the additional ternary systems $\text{NaBH}_4\text{--NaCl--H}_2\text{O}$ and $\text{NaBH}_4\text{--NaBr--H}_2\text{O}$.

We found no information in the literature on the study of the above systems. Only in the work of Stockmayer et al. [3] on the thermodynamic properties of sodium borohydride was there a report of the formation of solid solutions between $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ and the compounds $\text{NaBr} \cdot 2\text{H}_2\text{O}$ and $\text{NaI} \cdot 2\text{H}_2\text{O}$. At 0° sodium borohydride and sodium chloride and bromide separate from aqueous solutions as the dihydrates $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$, $\text{NaCl} \cdot 2\text{H}_2\text{O}$ and $\text{NaBr} \cdot 2\text{H}_2\text{O}$. Anhydrous NaBH_4 , NaCl, and NaBr crystallize above +36.4°, +0.15°, and +50.7°, respectively [4, 5].

The sodium borohydride used contained 99.0-99.4% of NaBH_4 (according to analysis for active hydrogen) and was obtained from the technical product by recrystallization from aqueous solution with subsequent extraction with liquid ammonia. The sodium chloride and bromide were of chemically pure grades and the water was freshly distilled. The solubility was studied under isothermal conditions; the composition of the solid phase was determined by Schreinemaker's method [6] and checked microscopically. The sodium borohydride content of the liquid phase and solid "residue" was determined by titration [1, 2]. The NaCl and NaBr were determined by titration with 0.1 N AgNO_3 solution by Mohr's method. To check that there was no hydrolysis of sodium borohydride in aqueous solutions of sodium halides, we also determined the NaBH_4 content of the liquid phase in parallel by the iodate method [7] and calculated the H/B ratio. This ratio remained constant as the halide concentration in the solution increased, and this confirms that there was no hydrolysis of NaBH_4 during the work.

The solubility isotherm at 0° for the ternary system $\text{NaBH}_4\text{--NaCl--H}_2\text{O}$ (Fig. 1), consists of two branches intersecting in a eutonic point B (25.5 weight % of NaBH_4 , 4.3 weight % of NaCl, and 70.2 weight % of H_2O). The bulk of the diagram is occupied by the crystallization field of anhydrous NaCl, indicating the high salting-

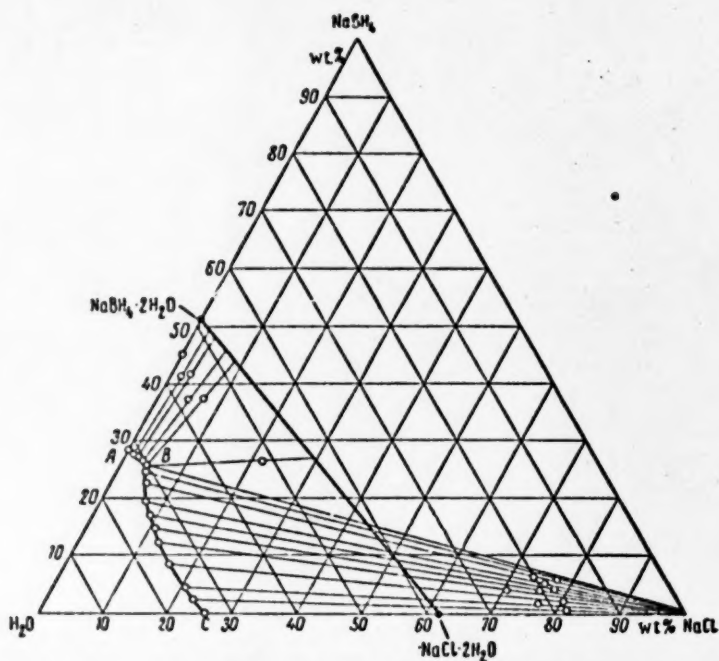


Fig. 1. Solubility isotherm of the system $\text{NaBH}_4\text{--NaCl--H}_2\text{O}$ at 0°C .

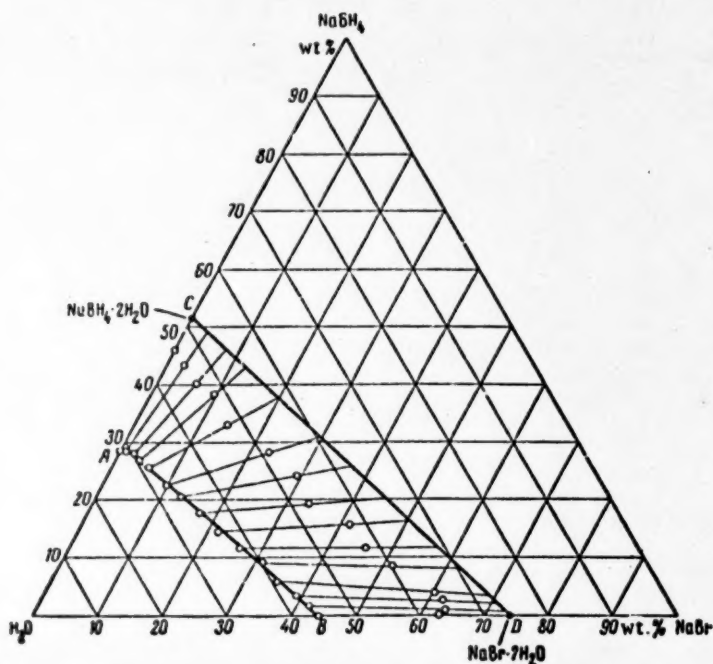


Fig. 2. Solubility isotherm of the system $\text{NaBH}_4\text{--NaBr--H}_2\text{O}$ at 0°C .

out power of sodium borohydride with respect to sodium chloride. While the "Schreinemaker rays" corresponding to the crystallization of anhydrous NaCl converged on one point well (Fig. 1), the rays corresponding to the

crystallization of the other solid phase diverged, and consequently the second branch of the solubility isotherm AB (from 0 to 4.3 weight % of NaCl) corresponds to crystallization of solid solutions based on sodium borohydride dihydrate, apparently with the composition $\text{Na}(\text{BH}_4, \text{Cl}) \cdot 2\text{H}_2\text{O}$.

The solubility isotherm at 0°C of the ternary system $\text{NaBH}_4\text{--NaBr--H}_2\text{O}$ (Fig. 2) shows the crystallization of only one solid phase, namely a continuous solid solution between $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaBr} \cdot 2\text{H}_2\text{O}$. The solubility of this solid solution falls steadily (almost linearly) from 28.3 weight % of NaBH_4 (point A) to 44.6% of NaBr (point B). The composition of the solid phase changes continuously from pure $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ (point C) to pure $\text{NaBr} \cdot 2\text{H}_2\text{O}$ (point D).

The results obtained confirm the similarity in the physicochemical properties of the borohydride ion and halide ions, which was pointed out by Stockmayer et al. [3]. Our data are also in agreement with the general rules of solid solution formation from the point of view of the ionic radii and polarizability coefficients of the corresponding ions.

The ionic radii of BH_4^- , Cl^- , and Br^- ions are 2.03 Å [9], 1.81 Å, and 1.96 Å [9] and the polarizability coefficients 3.94 Å^3 [10], 3.05 Å^3 , and 4.17 Å^3 [11], respectively. A comparison of the crystallochemical radii and polarizability coefficients shows that the borohydride ion is closer in its properties to bromide ion than to chloride ion. This may explain why $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaBr} \cdot 2\text{H}_2\text{O}$ form a continuous series of solid solutions at 0°C, while $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ and $\text{NaCl} \cdot 2\text{H}_2\text{O}$ form solid solutions only on the $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ side over a narrow range of concentrations (from 0 to ~8 weight % of NaCl).

The present work together with previous investigations [1, 2] show that the general rules of formation of the main forms of phase diagram in accordance with the physicochemical properties of the crystallizing of salts apply to a system involving the borohydride ion.

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ACETYL DERIVATIVES OF PENTAETHANODIFERROCENE

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We prepared mono- and diacetylpentaethanodiferrocenes, which are acylation products of the new aromatic compound pentaethanodiferrocene [2] that is formed by the reaction of ferrocene with 1,2-dichloroethane in the presence of anhydrous aluminum chloride. We found that the substance with m. p. 135° that we obtained previously in this reaction and called "diferrocenylethane" [1] is a mixture of isomers of 1,1-diferrocenylethane and a small amount of 1,2-diferrocenylethane.

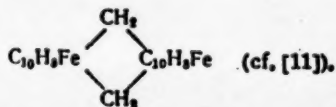
We were later able to isolate both isomers in an individual state by changing the method of treating the reaction products somewhat (see experimental section for details). Purification by chromatography on alumina in a mixture of benzene and n-heptane (1:1) yielded 1,1-diferrocenylethane with m. p. 147-148° [8] and 1,2-diferrocenylethane with m. p. 192-192.5°, which was identical with samples obtained by one of us and Kritskaya [4, 5]* and also one of us with É. G. Perevalova and Yu. T. Ustynyuk [6].

Acylation of pentaethanodiferrocene with acetic anhydride in the presence of 85% phosphoric acid gave the monoacetyl derivative, and acylation with acetyl chloride in the presence of anhydrous aluminum chloride in methylene chloride (solvent) gave diacetylpentaethanodiferrocene and other polyacetylpentaethanodiferrocenes.

Monoacetylpentaethanodiferrocene is a yellowish powder, which is readily soluble in alcohol, acetone, and benzene and less so in water and ether. It was recrystallized from absolute alcohol. Diacetylpentaethanodiferrocene is an orange-yellow powder and was recrystallized from n-heptane. The acylation confirmed the structure proposed previously for pentaethanodiferrocene.

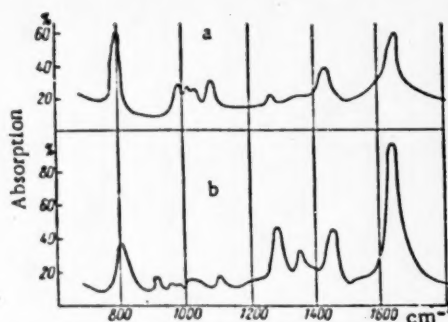
The infrared spectra of the acetyl derivatives contained a characteristic frequency in the region of 1670 cm^{-1} (carbonyl group), and also that of monoacetylpentaethanodiferrocene contained frequencies in the region of 1000 and 1100 cm^{-1} (free ferrocene ring); diacetylpentaethanodiferrocene did not show frequencies in the region of 1000 and 1100 cm^{-1} , and consequently the two acetyl groups enter different rings of pentaethanodiferrocene (see figure, b). Thus, the presence of two unsubstituted rings in pentaethanodiferrocene may be considered demonstrated.

* In this work [4, 5] and also the work of foreign authors [9, 10], 1,2-diferrocenylethane was obtained by the condensation of formaldehyde with ferrocene and was mistakenly taken to be the substance with the structure



Relative Chemical Displacements from Nuclear Magnetic Resonance Spectral Data

	H_{benzene}	H_0	H_{CH}	H_{CH_2}	H_{CH_3}	$H_{\text{CH}}-H_0$	$H_{\text{CH}_2}-H_0$	$H_{\text{CH}_3}-H_0$
Ferrocene	0	3,22	—	—	—	—	—	—
Ethylferrocene	0	3,34	—	5,35	6,56	—	2,02	3,22
Tributylferrocene	0	3,29	—	—	5,86	—	—	2,59
Pentaethanodiferrocene	0	3,29	—	5,35	—	—	2,16	—
Diisopropylferrocene [7]	2,72	5,97	7,36	—	8,86	1,39	—	2,89
1,1-Diferrocenylethane [8]		5,86	6,58	—	8,86	0,72	—	3,00
1,2-Diferrocenylethane								



Infrared spectra: a) monoacetyl pentaethanodiferrocene (0.0101 g in 0.8997 g of KBr); b) diacetyl pentaethanodiferrocene (0.0061 g in 0.7990 g of KBr).

In addition, we obtained new physicochemical data confirming the structure of pentaethanodiferrocene. The nuclear magnetic resonance spectra (see table) showed the absence of methyl groups from pentaethanodiferrocene and their presence in the standards, namely ethylferrocene [3] and 1,1-diferrocenylethane (cf. [9]).

Pentaethanodiferrocene and its acetyl derivatives are amorphous and do not have sharp melting points, but gradually darken and soften at about 100°. However, thermograms obtained on a PK-55 Kumakov pyrometer showed that the heating curve up to 200° has no exo- or endothermal effects.

The nuclear magnetic resonance spectra were kindly determined by Yu. Yu. Samitov; the infrared spectra were determined by N. A. Chumaevskii. The thermographic measurements were made by V. M. Kozhin and E. I. Yarem-bash, to whom the authors are very grateful.

Separation of reaction products from ferrocene and dichloroethane. The reaction of ferrocene (40 g, 0.21 mole) with dichloroethane (200 ml, 2.5 moles) in the presence of anhydrous aluminum chloride has been described by us previously.

After decomposition of the reaction mixture in the usual way and removal of the solvent, the reaction products were extracted with methanol in a Soxhlet apparatus. The solid residue from the Soxhlet thimble was treated with ether (50 ml per g of substance) and reprecipitated with methanol (10-fold excess). We obtained 1-2 g of pentaethanodiferrocene.

The residue which did not dissolve in this amount of ether was reprecipitated from benzene with a 10-fold amount of methanol. We obtained 1-2 g of a polymer with a molecular weight of 2300. All the mother solutions from the Soxhlet apparatus and solutions from reprecipitation of the samples from ether and benzene were evaporated to dryness without heating. The residue was chromatographed on alumina in a mixture of benzene and heptane (1:1) on a column 1 m high and 29 mm in diameter in 1-g portions with a flow rate of 5 ml/min. The fractions obtained were: I — an oil with n_D^{20} 1.6056 (3.17 g); II — ferrocene with m. p. 172° (5 g); III — 1,1-diferrocenylethane with m. p. 147-149° (1.05 g); IV — an intermediate fraction of oil + 1,1-diferrocenylethane (2.25 g); V — an oil with n_D^{20} 1.6530 (1.8 g); VI — 1,2-diferrocenylethane with m. p. 192-192.5° (0.1 g). The weight was 0.6 g.

Acetyl pentaethanodiferrocene $C_{30}H_{22}Fe_2-COCH_3$. A mixture of 2.5 g of pentaethanodiferrocene, 5 g of acetic anhydride, and 0.5 ml of 85% phosphoric acid was heated at 100-105° for 15 min. The mixture was then poured onto ice and the product washed with a solution of 4 g of sodium bicarbonate in 5 ml of water and then with water. The dark powder (2.6 g) was soluble in n-heptane, ether, acetone, and alcohol and less so in water. Recrystallization from absolute alcohol yielded a yellow powder, whose melting point in a sealed capillary was 105-110° (with decomp.).

Found %: C 70.87, 70.99; H 6.25, 6.23; Fe 20.51, 20.35. $C_{32}H_{32}Fe_2O$. Calculated %: C 70.60; H 5.80; Fe 20.15.

Molecular weight (cryoscopically in benzene): Found 529, $C_{32}H_{32}Fe_2O$. Calculated 544.28.

Diacetylpentaethanodiferrocene. To a solution of 2 g of pentaethanodiferrocene in 20 ml of methylene chloride was gradually added a solution of 0.65 ml of acetyl chloride and 1.04 g of anhydrous aluminum chloride in 20 ml of methylene chloride. Slight heat evolution was observed. The mixture was stirred at room temperature for 5 hr. After the reaction mixture had been kept overnight, it was poured onto a mixture of ice and HCl (1:1) and extracted with ether and benzene. All the solutions were combined, washed with 5% sodium carbonate solution and water, and dried with anhydrous sodium sulfate. Removal of the solvent in vacuum (20 mm) yielded 1.62 g of a dark red residue, which was chromatographed on silica gel in benzene to yield 0.3 g of an orange powder. It was recrystallized from n-heptane. It darkened above 80°C.

Found %: C 69.55; H 5.64; Fe 17.04. $C_{34}H_{34}Fe_2O_2$. Calculated %: C 69.60; H 5.85; Fe 19.10 (on Fe_2O_3).

Molecular weight (cryoscopically in benzene): Found 583, calculated for $C_{34}H_{34}Fe_2O$ 586.31. In addition, a mixture of isomers of triacetylpentaethanodiferrocene and tetraacetylpentaethanodiferrocene was obtained.

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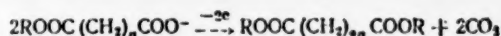
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SYNTHESIS OF 1,14-TETRADECANEDICARBOXYLIC AND 1,15-PENTADECANEDICARBOXYLIC ACIDS

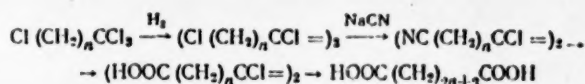
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The most efficient methods of synthesizing high-molecular α, ω -dicarboxylic acids are the electrolysis of salts of dicarboxylic half-esters [1]

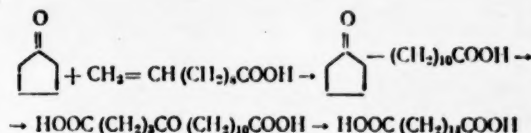


and reductive dimerization of $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes [2]



Kharasch et al. [3] showed that the irradiation of a mixture of cyclohexanone and 1-octene with ultraviolet light gave 2-octylcyclohexanone in 20-30% yield.

As a result of a detailed study of the free-radical addition of acids and alcohols to α -olefins, we found the optimal conditions for obtaining adducts in high yields [4]. Making use of these conditions, in the present investigation we added cyclopentanone and cyclohexanone to undecylenic acid in the presence of tert-butyl peroxide. The reactions were carried out with the molar proportion of ketone: undecylenic acid: peroxide = 3:0.3:0.06 at 130-132° with cyclopentanone and 151-153° with cyclohexanone. The acid and peroxide were added to the ketone dropwise over a period of 6-6.5 hr. The yield of 1:1 adduct with cyclopentanone was 69.5% and with cyclohexanone, 50%. 11-(2'-Ketocyclopentyl)-undecanoic acid was oxidized to 5-ketotetradecane-1,14-dicarboxylic acid, and the latter was reduced with hydrazine hydrate to 1,14-tetradecanedicarboxylic acid.



1,15-Pentadecanedicarboxylic acid was obtained analogously from 11-(2'-ketocyclohexyl)-undecanoic acid.

EXPERIMENTAL

11-(2'-Ketocyclopentyl)-undecanoic acid. Over a period of 6.5 hr, a solution of 55.3 g (0.3 mole) of undecylenic acid and 8.8 g (0.06 mole) of peroxide in 52.3 g (0.6 mole) of cyclopentanone was added to 200 g

(2.4 moles) of cyclopentanone at 130-132°. The reaction mixture was heated for a further 2 hr and then distilled to yield 5 g of unreacted undecylenic acid, 56 g of 11-(2'-ketocyclopentyl)-undecanoic acid, and 16 g of residue. The yield of 11-(2'-ketocyclopentyl)-undecanoic acid, calculated on the undecylenic acid taken, was 69.5%, and it had b. p. 213-220° (2 mm) and m. p. 51.6-52° (from acetone).

Found %: C 71.46, 71.36; H 10.50, 10.30. $C_{16}H_{24}O_3$. Calculated %: C 71.60; H 10.51.

The semicarbazone had m. p. 166.5-167.5° (from alcohol).

Found %: C 62.56, 62.69; H 9.51, 9.57. $C_{17}H_{23}O_3N_3$. Calculated %: C 62.74; H 9.60.

5-Ketotetradecane-1,14-dicarboxylic acid. The oxidation conditions were those developed by V. V. Korshak et al. [5]. To a solution of 50 g of sulfuric acid in 85 ml of water at 55° was added 55 g (0.205 mole) of molten 11-(2'-ketocyclopentyl)-undecanoic acid with vigorous stirring, and then a solution of 31 g of chromium trioxide and 50 g of sulfuric acid in 50 ml of water was introduced over a period of 20 min at the same temperature (cooling). The reaction mixture was stirred at 55° for a further 3 hr. The solid mass was then separated from the liquid on a Buchner funnel and dissolved in acetone, the acetone solution filtered, and the filtrate evaporated. The precipitated acid was separated from the mother solution and redissolved in acetone and the acetone solution decanted, filtered, and evaporated. The 5-ketotetradecane-1,14-dicarboxylic acid obtained was recrystallized from benzene. The yield was 74% (45.6 g) and the m. p. 123.5-123.8°.

Found %: C 63.76, 63.49; H 9.38, 9.35. $C_{16}H_{28}O_5$. Calculated %: C 63.97; H 9.40.

The semicarbazone melted with decomposition at 134°.

Found %: C 56.14; H 8.81. $C_{17}H_{21}O_5N_3$. Calculated %: C 57.12; H 8.74.

1,14-Tetradecanedicarboxylic acid. To a solution of 8.5 g of NaOH and 8.5 ml of hydrazine hydrate in 75 ml of diethylene glycol was added 7.5 g (0.025 mole) of 5-ketotetradecane-1,14-dicarboxylic acid. The mixture was heated for 2 hr at 142° and then for a further 4 hr at 210° after the removal of excess hydrazine hydrate and water. To the cooled reaction mixture was added 50 ml of water and hydrochloric acid to a weakly acid reaction. The liquid phase was separated by filtration from the 1,14-tetradecanedicarboxylic acid formed, which was obtained in 88% yield (6.3 g) after recrystallization and had m. p. 126° (from acetone).

Found %: C 66.98, 66.81; H 10.56, 10.48. $C_{16}H_{30}O_4$. Calculated %: C 67.10; H 10.56.

Literature data [6]: m. p. 124-124.2°.

11-(2'-Ketocyclohexyl)-undecanoic acid. Over a period of 6 hr, a solution of 55.3 g (0.3 mole) of undecylenic acid and 8.8 g (0.06 mole) of peroxide in 55 g (0.56 mole) of cyclohexanone was added to 240 g (2.44 moles) of cyclohexanone at 151-153°, and then the reaction mixture was heated at the same temperature for a further 2 hr. Vacuum distillation of the reaction mixture yielded 18.5 g of unreacted undecylenic acid, 42.7 g of keto acid, and 13 g of residue. The yield of 11-(2'-ketocyclohexyl)-undecanoic acid, calculated on the undecylenic acid taken, was 50% and on that reacting, 75%, and the m. p. was 64° (from acetone).

Found %: C 72.11, 79.09; H 10.71, 10.60. $C_{17}H_{30}O_3$. Calculated %: C 72.30; H 10.70.

The semicarbazone had m. p. 135-136° (from alcohol).

Found %: C 63.72, 63.85; H 10.03, 10.06. $C_{18}H_{33}O_3N_3$. Calculated %: C 63.68; H 9.80.

6-Ketopentadecane-1,15-dicarboxylic acid. The oxidation of 11-(2'-ketocyclohexyl)-undecanoic acid (at 65°) and the isolation of the 6-ketopentadecane-1,15-dicarboxylic acid formed from the reaction mixture were the same as in the preparation of 5-keto-tetradecane-1,14-dicarboxylic acid. The yield 6-ketopentadecane-1,15-dicarboxylic acid was 78% and the m. p. was 109.5-110.5° (from benzene).

Found %: C 65.19, 65.12; H 9.78, 9.68. $C_{17}H_{30}O_5$. Calculated %: C 64.96; H 9.62.

The semicarbazone had m. p. 161-161.3° (from alcohol).

Found %: C 58.16, 58.20; H 9.08, 9.03. $C_{19}H_{33}O_5N_3$. Calculated %: C 58.20; H 8.96.

1,15-Pentadecanedicarboxylic acid. To a solution of 6.6 g of NaOH and 7 ml of hydrazine hydrate in 60 ml of ethylene glycol was added 6.3 g (0.02 mole) of 6-ketopentadecane-1,15-dicarboxylic acid. The rest of the synthesis was analogous to that of 1,14-tetradecanedicarboxylic acid.

We obtained 5.6 g (93%) of 1,15-pentadecanedicarboxylic acid with m. p. 119° (from acetone).

Found %: C 67.53, 67.66; H 10.63, 10.72. $C_{17}H_{32}O_4$. Calculated %: C 67.96; H 10.74.

Literature data [6]: m. p. 118°.

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METHOD OF DETERMINING THE COMPOSITION OF AN EXTRACTED COMPLEX

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The concept of extraction rays, i.e., lines along which the composition of the aqueous phase changes during extraction, has been introduced into work on diagrams of multicomponent extraction systems [1-3]. An extraction ray begins at a composition point corresponding to the concentration of the starting solution and ends in a point corresponding to one of the compositions of the equilibrium aqueous phase.

In examining the form of the extraction ray in four-component systems of the type substance extracted-salting-out agent-water-extractant, we make the following assumptions:

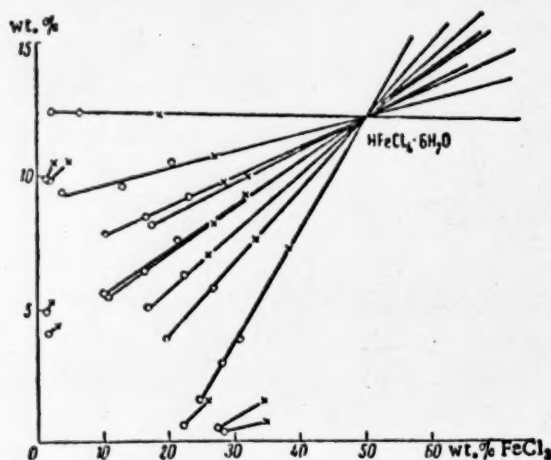
- 1) The organic extractant is practically insoluble in the aqueous phase, whose composition therefore lies within the limits of a three-component system.
- 2) In a certain region of the diagram (in the layer-formation region in our case) the organic phase extracts only one compound of definite composition (the number of molecules of extractant incorporated in the extracted complex is not considered).

Then it is easily shown that when the composition of the aqueous phase is expressed in weight (or molecular) percents, the extraction rays will be straight lines intersecting in a point corresponding to the composition of the complex extracted. Thus, a study of the extraction rays is a method of establishing the composition of the form extracted. The method of determining the composition of the extracted form proposed here is essentially analogous to Schreinemakers's residue method, which is used for determining the composition of the solid phase in three-component systems, and therefore has all the same merits.

We used this method for determining the composition of the extracted form in the system $\text{FeCl}_3\text{--HCl--H}_2\text{O--}(\text{C}_2\text{H}_5)_2\text{O}$, which was studied previously [4].

The second of the above assumptions means that the true extraction of water, hydrochloric acid, and ferric chloride into the ether phase in the region of applicability of this method should be low in comparison with their extraction in the form of the complex $\text{mFeCl}_3 \cdot \text{nHCl} \cdot \text{pH}_2\text{O}$. This evidently occurs only during extraction from solutions with high concentrations of hydrochloric acid and ferric chloride. At the origin of the coordinates (where the true extraction of water is high) and close to both coordinate axes (where the true extraction of FeCl_3 and HCl cannot be neglected) there should therefore be curvature of the extraction rays. In work with concentrated solutions, the true extraction of water and HCl may be decreased by preliminary saturation of the ether with hydrochloric acid solution of appropriate concentration. Extraction rays obtained in this way are illustrated in the figure.

As the figure shows, a considerable number of the extraction rays are linear and intersect in one point, which corresponds to the composition $\text{HFeCl}_4 \cdot 6\text{H}_2\text{O}$ for the extracted complex. There is also curvature of the



Extraction rays in the system $\text{FeCl}_3\text{--HCl--H}_2\text{O--}(\text{C}_2\text{H}_5)_2\text{O}$.

extraction rays in regions adjacent to the coordinate axes. Thus, $\text{HFeCl}_4 \cdot 6\text{H}_2\text{O}$ is only the dominating form in which ferric chloride passes into the ether phase in a considerable region of compositions. With an inadequate concentration of any of the components in the aqueous phase, the ether phase is also impoverished in the corresponding component.

We established that there is predominant extraction of the ferric chloride into diethyl ether in the form of $\text{HFeCl}_4 \cdot 6\text{H}_2\text{O}$, which agrees with the data of other authors, obtained by different methods. The idea of the extraction of ferric chloride from hydrochloric acid solutions in the form of the complex acid HFeCl_4 is generally accepted [5]. The ratio of $\text{FeCl}_3\text{:H}_2\text{O}$ in the organic phase is 1:4.5-6 according to the data of various authors [4-6].

We consider that the method described here for determining the composition of the extracted form involves the minimal number of arbitrary assumptions and therefore may find wide application in the study of extraction equilibria.

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INFRARED SPECTRA OF UNSYMMETRICAL DIACYL PEROXIDES

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In a number of cases, the interpretations of frequencies of infrared absorption spectra of organic peroxides given in the literature are contradictory and doubtful.

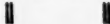
Shreve et al. [1] reported that phthaloyl, p-chlorobenzoyl, and benzaldehyde peroxides have a strong absorption band with a frequency of about 1000 cm^{-1} . On the other hand, di-tert-butyl peroxide absorbs at 880 cm^{-1} . These data were confirmed in [2]. The authors of [1, 2] consider that the absorption bands mentioned are characteristic of vibrations of the $-\text{O}-\text{O}-$ group of aromatic and aliphatic peroxide compounds.

The attempts of other investigators [3-5] to find the characteristic absorption of $-\text{O}-\text{O}-$ bonds in organic peroxides did not give positive results.

The infrared spectra of compounds containing the hydroperoxide group ROOH have been studied in more detail [1, 6-8]. A preliminary interpretation of the spectra of four unsymmetrical diacyl peroxides was given in [9].

However, literature data are inadequate for the detection of organic peroxides formed during an oxidation by infrared spectra, especially as the presence of the frequencies 880 and 1000 cm^{-1} does not unequivocally indicate the presence of a peroxide group $\text{O}-\text{O}$, whose vibrations are not characteristic [10].

More experimental material is required to establish the rules of the spectral manifestation of the vibrations of a $-\text{C}-\text{O}-\text{O}-\text{C}-$ group in peroxides of



the form $\text{R}-\text{C}-\text{O}-\text{O}-\text{C}-\text{R}'$. It is very profitable to



follow the changes in the infrared spectra occurring during the oxidation and the formation of peroxides.

With this aim we studied the infrared spectra of four unsymmetrical diacyl peroxides: acetyl p-chlorobenzoyl, acetyl m-chlorobenzoyl, acetyl o-chlorobenzoyl,

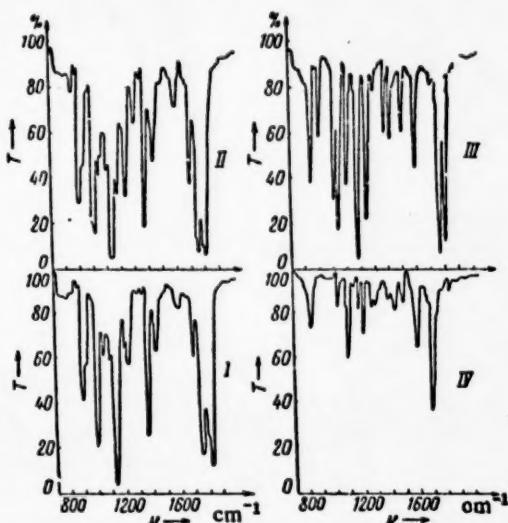


Fig. 1. Transmission spectra of CCl_4 solutions of a mixture of p-chlorobenzaldehyde and acetic anhydride: before oxidation (I); after oxidation for 3 hr (II); 0.1 M CCl_4 solution of acetyl p-chlorobenzoyl peroxide obtained during the oxidation (III); 0.1 M CCl_4 solution of p-chlorobenzaldehyde (IV).

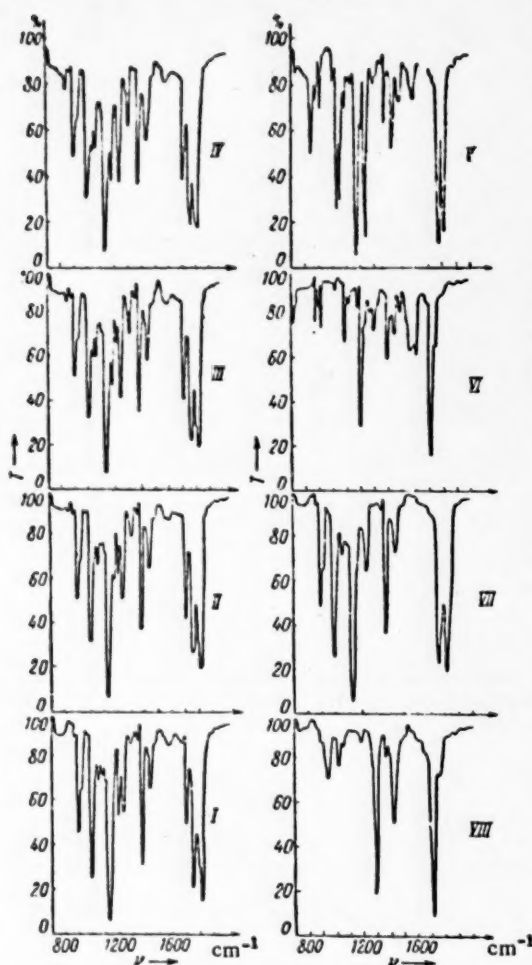


Fig. 2. Transmission spectra of CCl_4 solutions of m-chlorobenzaldehyde and acetic anhydride: before oxidation (I); after oxidation for 2 hr (II); after oxidation for 4 hr (III); after oxidation for 6 hr (IV); 0.1 M solution in CCl_4 obtained during the oxidation of acetyl m-chlorobenzoyl peroxide (V); 0.1 M CCl_4 solution m-chlorobenzaldehyde (VI); 0.1 M CCl_4 solution of acetic anhydride (VII); 0.1 M CCl_4 solution of acetic acid (VIII).

to acetic acid, which was formed together with peroxide during the oxidation. This was confirmed by the fact that the spectrum of acetic acid has a very intense absorption band at 1300 cm^{-1} (Fig. 2, VIII). In addition, the spectrum of acetic acid contains a very intense band with a maximum at 1710 cm^{-1} , belonging to $\text{C}=\text{O}$ vibrations.

The starting aldehydes also have the absorption band of a carbonyl group in the same region of the spectrum ($1704\text{--}1710\text{ cm}^{-1}$). The intensity of the absorption band of the carbonyl group of the starting aldehydes should have decreased during the oxidation. However, the intensity of this band increased somewhat during the oxidation, though this was slight and also indicates the formation of acetic acid in the oxidation mixture.

and propionyl benzoyl peroxides. The spectra of the first three peroxides and also the starting aldehydes and anhydrides (Figs. 1, 2, and 3) in the transmission region of an NaCl prism were obtained with an IKS-14 spectrometer. We examined 0.1 M solutions of the peroxides in CCl_4 with an absorbing layer thickness of 0.25 mm. The spectra of propionyl benzoyl peroxide (Fig. 4) were obtained on an IKS-11 with an absorbing layer thickness of 0.1 mm. The infrared spectra of acetyl o-chlorobenzoyl and propionyl benzoyl peroxides were examined for the first time.

The figures show that new bands which were absent from the spectra of unoxidized samples and also the starting aldehydes and anhydrides appeared in the spectra during the oxidation of the samples. These included a band of low intensity at $845\text{--}860\text{ cm}^{-1}$ (Fig. 1, II, Fig. 2, II-IV, and Fig. 3, II-IV), which was observed in the spectra of all the given peroxides. During the oxidation of the samples, two bands appeared in the regions of $1000\text{--}1030\text{ cm}^{-1}$ and $1030\text{--}1050\text{ cm}^{-1}$, which were very well expressed in the spectra of the peroxides. The intensity of the band in the region of $1030\text{--}1050\text{ cm}^{-1}$ depended on the position of the substituent in the ring and its appearance in the spectrum evidently was not connected with the formation of the peroxide chain, but was more probably due to out-of-plane vibrations of the benzene ring. Acetyl p-chlorobenzoyl (Fig. 1, III), acetyl m-chlorobenzoyl (Fig. 2, V), and acetyl o-chlorobenzoyl (Fig. 3, V) peroxides have a very intense absorption band with a maximum at 1175 cm^{-1} , which appeared in the spectrum during oxidation. The intensity and wavelength of the absorption maximum were independent of the position of the substituent in the ring. There was no absorption in this region in the spectrum of propionyl benzoyl peroxide (Fig. 4, IV). Hence we may conclude that the frequency mentioned should be ascribed to vibrations of the $-\text{C}-\text{CH}_3$ group at the end of the chain.

The appearance of absorption bands in the region of $1220\text{--}1236\text{ cm}^{-1}$, which are very intense in the spectra of all the pure peroxides but are absent from those of the starting aldehydes and anhydrides, during the oxidation shows very clearly on all the figures. At the same time, an absorption band with a maximum at 1300 cm^{-1} appeared (Fig. 1, II, Fig. 2, II-IV, and Fig. 3, II-IV). The absorption band at 1300 cm^{-1} belonged

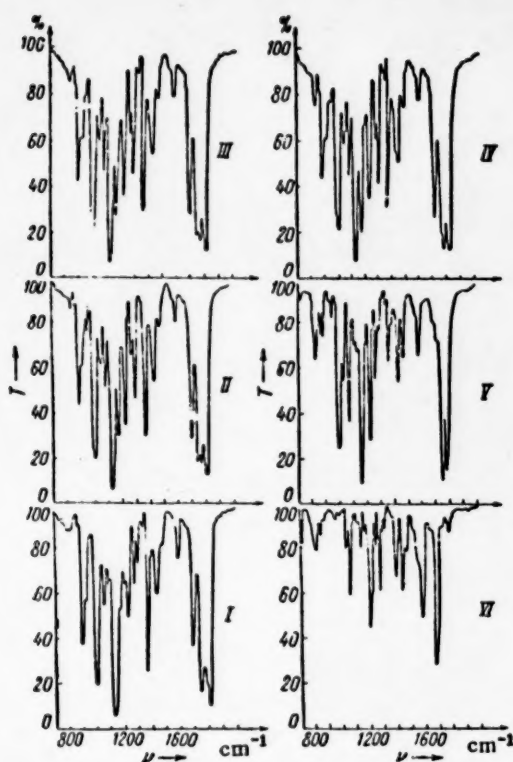


Fig. 3. Transmission spectra in CCl_4 solutions in a mixture of *o*-chlorobenzaldehyde and acetic anhydride; before oxidation (I); after oxidation for 20 min (II); after oxidation for 40 min (III); after completion of oxidation (IV); 0.1 M CCl_4 solution obtained during the oxidation of acetyl *o*-chlorobenzoyl peroxide (V); 0.1 M CCl_4 solution of *o*-chlorobenzaldehyde (VI).

During the oxidation, new bands appeared in the spectra of the samples with maxima at $1770\text{--}1774\text{ cm}^{-1}$ and $1800\text{--}1805\text{ cm}^{-1}$ and these were very intense in the spectra of the peroxides and belonged to $\text{C}=\text{O}$ vibrations.

In the spectral region of $1300\text{--}1750\text{ cm}^{-1}$, there was a change in the intensities of bands with maxima at $1375\text{--}1380\text{ cm}^{-1}$ and $1445\text{--}1450\text{ cm}^{-1}$ during the oxidation of the samples. These bands were observed in the spectra of the starting aldehydes and anhydrides and may be assigned to symmetrical and antisymmetrical deformation vibrations of $\text{C}-\text{CH}_3$ and CH_2 groups.

The spectra of all the peroxides showed a very weak absorption band in the region of $1580\text{--}1630\text{ cm}^{-1}$. It was shown by samples before oxidation, underwent no appreciable changes during the oxidation, and was also observed in the spectra of all the starting aldehydes. The position of its maximum changed, though only slightly, with the position of the substituent in the ring. It should probably be ascribed to vibrations of the benzene ring. It is difficult to interpret the band in the region of $1075\text{--}1100\text{ cm}^{-1}$. Its intensity was high in the spectra of acetyl *p*-chlorobenzoyl and acetyl *m*-chlorobenzoyl peroxides and low in the spectrum of acetyl *o*-chlorobenzoyl peroxide. It was not formed during the oxidation and was present in the spectra of the starting aldehydes for the above three peroxides.

In considering the experimental data obtained it should be noted that the absorption bands with maxima in the regions of $845\text{--}860$, $1000\text{--}1030$, and $1220\text{--}1236\text{ cm}^{-1}$, whose formation occurs during the oxidation, are evidently connected with the formation of a peroxide chain of the form $-\text{C}-\text{O}-\text{O}-\text{C}-$. As was mentioned

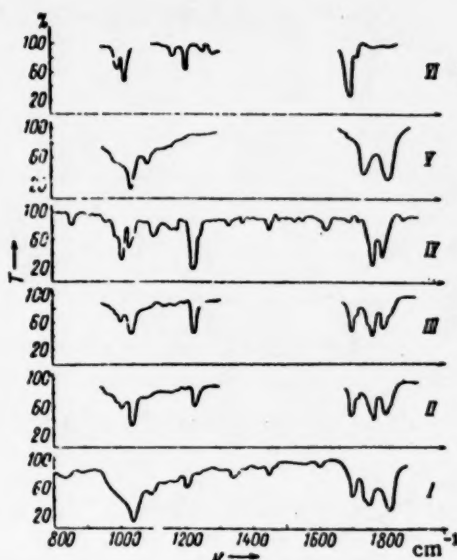


Fig. 4. Transmission spectra of CCl_4 solutions of a mixture of benzaldehyde and propionic anhydride; before oxidation (I); after oxidation for 2.5 hr (II); after oxidation for 5 hr (III); 0.1 M CCl_4 solution obtained during the oxidation of propionyl benzoyl peroxide (IV); 0.1 M CCl_4 solution of propionic anhydride, in the regions of $950\text{--}1300$ and $1670\text{--}1900\text{ cm}^{-1}$ (V); 0.1 M CCl_4 solution of benzaldehyde in the regions of $950\text{--}1050$, $1100\text{--}1300$, and $1670\text{--}1900\text{ cm}^{-1}$ (VI).

The spectra of all the samples before oxidation contained two very intense bands with maxima at $1757\text{--}1760\text{ cm}^{-1}$. These bands belonged to $\text{C}=\text{O}$ vibrations of the starting anhydrides (Fig. 2, VII and Fig. 4, V).

above, the authors of [1, 2] assigned the band in the region of 1000 cm^{-1} to vibrations of the $-\text{O}-\text{O}-$ bond of aromatic peroxides and the band at 880 cm^{-1} to the same bond of aliphatic peroxides. In our opinion, this interpretation is unconvincing. The existence of quite characteristic bands of $-\text{O}-\text{O}-$ vibrations of peroxides of the type $\text{R}-\text{C}-\text{O}-\text{O}-\text{C}-\text{R}'$ is improbable. It is more natural to assume that the appearance of these bands is

$$\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ \text{R}-\text{C}-\text{O}-\text{O}-\text{C}-\text{R}' \end{array}$$

connected with vibrations of the chain as a whole and not the $-\text{O}-\text{O}-$ bond alone. It is probable that those bands which are particularly intense in the regions of $1000-1030$ and $1220-1236\text{ cm}^{-1}$ are characteristic of a chain of the form $-\text{C}-\text{O}-\text{O}-\text{C}-$ of the given class of compound. We will continue the study of the infrared

spectra of other peroxides.

The authors would like to thank Prof. Yu. A. Ol'dekop, G. S. Bylina, and N. E. Nesterovich for providing the compounds.

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STEPWISE DEHYDRATION OF GLYCOLS ON A TRICALCIUM PHOSPHATE CATALYST

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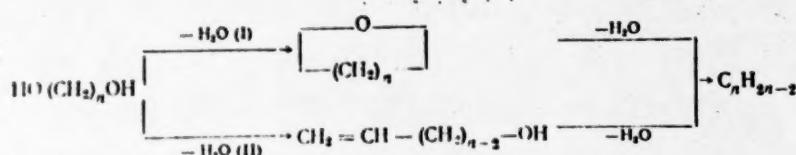
Original article submitted September 10, 1960

The catalytic dehydration of dihydric alcohols, in contrast to monohydric alcohols, has been studied little. Allyl alcohol and isomerization, disproportionation, and other products were obtained from trimethylene glycol at 250-350° over Al_2O_3 . Trimethylene oxide was detected [1]. The complete dehydration of butane-1,4-diol is catalyzed by Al_2O_3 , Cr_2O_3 , CaCl_2 , CaHPO_4 , and Na_3PO_4 on charcoal [2], and partial dehydration to tetrahydrofuran is catalyzed by cation-exchange resins [3], acids [4], phosphates, chlorides, etc. [5]. But-2-ene-1,4-diol is dehydrated to dihydrofuran in the presence of acids, Al_2O_3 , ThO_2 , and AlPO_4 [6]. Pentane-1,5-diol is dehydrated on phosphorus to 1,3-pentadiene in 37% yield, and tetrahydrofuran is formed in 42% yield on Al_2O_3 and kaolin [7]. Tetrahydropyran is formed on ion-exchange resins [3]. Hexane-1,6-diol was converted to α -methyl-tetrahydropyran by concentrated sulfuric acid [8] and hexamethylene oxide by 57% H_2SO_4 [9].

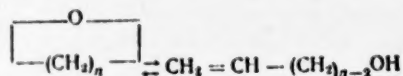
In the present work we studied the dehydration of a series of diols over a wide temperature range under the same conditions on the same catalyst. In parallel, we studied the dehydration of possible intermediate products, namely oxacyclanes and unsaturated alcohols. The results obtained make it possible to assess the effect of the structure of the glycols on the direction of the reaction, to determine the conditions under which they undergo only partial dehydration to oxides, and to find the routes of their complete dehydration to dienes.

Over the temperature range of 280-320°, C_4 and C_5 glycols are dehydrated selectively to the corresponding oxides. Figure 1A shows that the ease of formation of oxacyclanes falls in the series $\text{C}_4 > \text{C}_5 > \text{C}_6$. Tetrahydrofuran is obtained in a higher yield and at a lower temperature than tetrahydropyran, which is obtained more readily than hexamethylene oxide. Unsaturated alcohols and diolefins are also formed above 320°.

The strain of oxacyclanes (in kcal/mole) is 4.6 for C_4 and 0 for C_5 . For C_3 and C_6 it is probably close to the strain in thiacyclanes, which equals 19.8 for C_3 and 3.9 for C_6 [10]. However, as Fig. 1C shows, the degree of dehydration of C_4 and C_5 oxacyclanes was found to be approximately the same under the same conditions, while it was appreciably higher for C_6 . A comparison of Figs. 1B and 1C shows that oxacyclanes are more difficult to dehydrate to diolefins than the corresponding glycols. The dehydration of tetrahydrofuran to butadiene begins at a temperature 100° above that at which butanediol is dehydrated to butadiene. Analogously, tetrahydropyran is more difficult to dehydrate to pentadienes than pentane-1,5-diol. As Fig. 2C shows, the maximum yield of hexenol, 17% (curve 2), was obtained at 350°; of hexamethylene oxide, 32% (curve 1), at 380°; and of hexadienes, 60% (curve 3), at 400°. The rapid formation of diolefin at temperatures above 350° with a simultaneous increase in the yield of hexamethylene oxide and a decrease in the yield of hexenol shows that the diolefin is formed largely from hexenol, which is less stable than the oxide. In actual fact, when hexenol was passed over the catalyst at 400°, the degree of conversion to hexadiene was 75-80%, and with hexamethylene oxide under the same conditions the degree of conversion was 18%. Thus, the formation of diolefins in this process proceeds predominantly through the stage of unsaturated alcohols (II) and not through the stage of oxacyclanes (I).



As regards the unsaturated alcohol, it may be formed either by isomerization of the oxacyclanes:



or by direct dehydration of the diol. In our experiments at 340° and above, diolefins were formed from oxacyclanes, and unsaturated alcohols were not detected. In the dehydration of glycols under the same conditions, unsaturated alcohols were obtained together with diolefins. Therefore, it must be assumed that at elevated temperatures there is a change in the reaction mechanism, and there appears direction II, which has a considerably higher temperature coefficient than I. In the case of pentanediol, the temperature coefficient of reaction (II) is relatively low, and therefore the rate of formation of diolefin is less than from C₄ and C₆ diols (Fig. 1B).

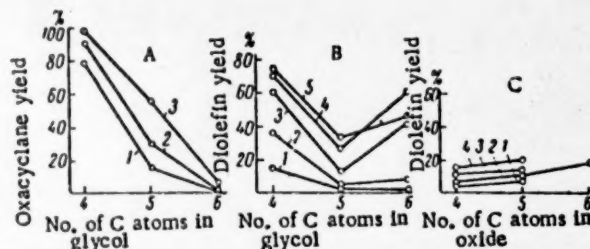


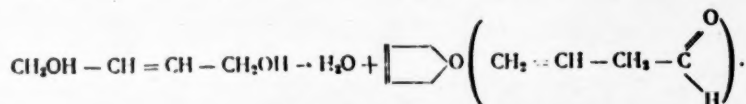
Fig. 1. Dehydration of C₄, C₅, and C₆ glycols: A) to oxacyclanes at 280° (1), 300° (2), and 320° (3); B) to diolefins at 335° (1), 350° (2), 380° (3), 410° (4), and 420° (5); C) dehydration of oxacyclanes to diolefins at 390° (1), 400° (2), 410° (3), and 420° (4).

EXPERIMENTAL

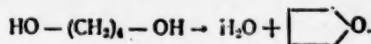
The experiments were carried out under flow conditions in a quartz tube. The catalyst volume was 25 ml and the grain size 2 x 3 mm. The preparation of the catalyst was described in [11]. The diols (oxacyclanes and unsaturated alcohols) were passed through steadily at a rate of 17.5 ml/hour. The liquid reaction products were dried over baked potassium carbonate and fractionated on a column of 15 theoretical plates. Their contents of carbonyl groups and unsaturated bonds were determined. The position of the double bonds was determined by means of the Raman spectrum. The yield was calculated on the amount of compound passed.

Dehydration of trimethylene glycol (b. p. 95°/5 mm, n_D^{20} 1.4396). Its degree of conversion at 250, 300, 350° was 5, 20, and 49%, respectively. The main reaction products were allyl alcohol (b. p. 96-97°, d_4^{20} 0.8569, n_D^{20} 1.4136) and propionaldehyde (b. p. 47-49°, d_4^{20} 0.7970, n_D^{20} 1.3644). Trimethylene oxide was not detected.

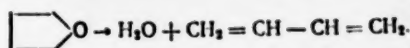
Dehydration of but-2-ene-1,4-diol (b. p. 115-122°/8 mm, d_4^{20} 1.067, n_D^{20} 1.4732). At 280°, the degree of conversion was 60%. The main reaction products were 2,5-dihydrofuran (b. p. 66-67°, d_4^{20} 0.9560, n_D^{20} 1.4275, 25.8% yield) and crotonaldehyde (b. p. 102-103°, d_4^{20} 0.8519, n_D^{20} 1.4370, 11.5% yield).



Dehydration of butane-1,4-diol (b. p. 106°/5 mm, d_4^{20} 1.015, n_D^{20} 1.4478), Fig. 2A. Over the range of 260-320°, only tetrahydrofuran (b. p. 64-65°, d_4^{20} 0.8878, n_D^{20} 1.4075) was formed and its yield reached 98% (curve 1).



At higher temperatures, the yield of tetrahydrofuran fell and there were also formed butadiene (determined chromatographically), but-1-en-4-ol (b. p. 113-115°, d_4^{20} 0.8460, n_D^{20} 1.4244), but-2-en-4-ol, and butyraldehyde. At 336°, the yield of gaseous products was 14% and at 426°, 73% if the gas was taken as butadiene (Fig. 2, 2). In the experiment at 425°, the gaseous products were found to contain 73% of butadiene. Tetrahydrofuran was recovered completely at 340°. Its dehydration to butadiene began at temperatures above 380° (curve 3):



At 380-494°, the liquid catalyzate was found to contain only tetrahydrofuran and water.

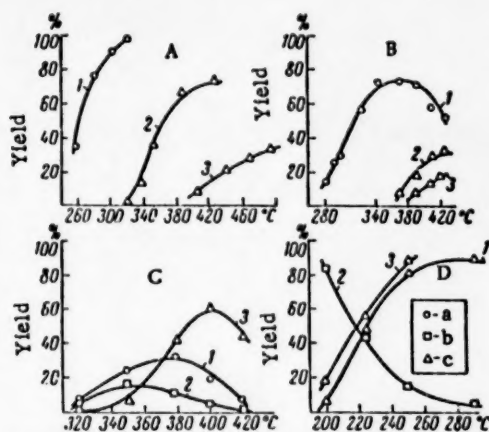
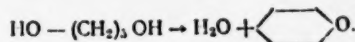
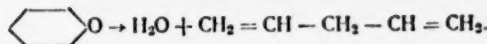


Fig. 2. Dehydration of butane-1,4-diol and tetrahydrofuran (A), pentane-1,5-diol and tetrahydropyran (B), hexane-1,6-diol (C), and 3,7-dimethyloctane-1,7-diol and citronellol (D): a) oxacyclanes; b) unsaturated alcohols; c) diolefins.

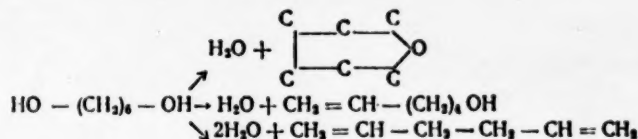
Dehydration of pentane-1,5-diol (b. p. 115°/5 mm, d_4^{20} 0.9850, n_D^{20} 1.4512), Fig. 2B. Over the range of 280-343°, pentanediol was dehydrated selectively to tetrahydropyran (b. p. 86.5-87.5°, d_4^{20} 0.8634, n_D^{20} 1.4280), curve 1:



Its yield at 343° was 72%. At higher temperatures there were also formed pentenols (b. p. 135-139°, d_4^{20} 0.8412, n_D^{20} 1.4377) and pentadienes (I, b. p. 23-26°, n_D^{20} 1.3895, Raman spectral frequency 1647.3 cm^{-1} ; II, b. p. 41-42°, n_D^{20} 1.4320, Raman spectral frequency 1651.1 cm^{-1} ; during hydrogenation the diene absorbed ~2 moles of H_2), curve 2. At 423° the yield of pentadienes was 33%. Pentanediol was unchanged at this temperature in the absence of catalyst. Tetrahydropyran formed pentadienes at 389-418° (curve 3):

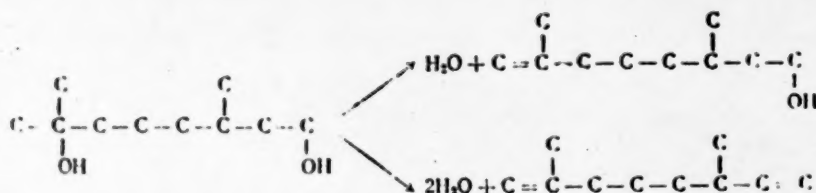


Dehydration of hexane-1,6-diol (b. p. 127°/5 mm, m. p. 40°), Fig. 2C. The reaction products were hexamethylene oxide (curve 1) (b. p. 119-120°, d_4^{20} 0.9037, n_D^{20} 1.4394, C 71.59%, H 12.00%, infrared spectrum as in [12]), hexenols (b. p. 155-158°, d_4^{20} 0.8418, n_D^{20} 1.4375, Raman spectral frequencies 1642 cm^{-1} and 1678 cm^{-1}), curve 2, and 1,5-hexadiene (b. p. 61-64°, d_4^{20} 0.7031, n_D^{20} 1.4110; 2 moles of H_2 were absorbed during hydrogenation; Raman spectral frequency 1642 cm^{-1}), curve 3.



The following isomerization products were formed simultaneously: α -methyltetrahydropyran, α -ethyltetrahydropyran, 1,4-hexadiene, etc.

Dehydration of 3,7-dimethyloctane-1,7-diol (b. p. 133°/4 mm, d_4^{20} 0.9274, n_D^{20} 1.4609), Fig. 2D. The reaction was carried out in vacuum (20 mm), the amount of catalyst was 100 ml, and the diol was passed at 90 ml/hr. At 200°, the diol was dehydrated selectively to citronellol (b. p. 128-129°/22 mm, d_4^{20} 0.8547, n_D^{20} 1.4609), curve 1, in 84% yield. The yield of the diolefin (b. p. 162-164°, d_4^{20} 0.7984, n_D^{20} 1.4522, Raman spectral frequencies 1644 cm^{-1} and 1669 cm^{-1}) was 5%:



With a rise in temperature the yield of citronellol fell and that of the diolefin increased correspondingly (curve 2) and reached 90% at 290°. Under similar conditions, citronellol was dehydrated to diolefins in approximately the same yield as the diol (curve 3).

Thus, dehydration of C_4 , C_5 , and C_8 α, ω -glycols proceeds in stages. An oxacyclane is formed in the first stage of the process. In the second stage there is also formed the isomeric unsaturated monohydric alcohol. The final product of diol dehydration, a diolefin, is obtained mainly through the formation of the unsaturated alcohol (II) and not through the oxide (I).

But-2-ene-1,4-diol is dehydrated mainly to form the oxide. The corresponding oxides were not detected in the dehydration products of C_3 and C_8 diols. However, in analogy with [1], it is possible that trimethylene oxide is formed during the dehydration of trimethylene glycol, but isomerizes rapidly to allyl alcohol and propionaldehyde. The oxide was not formed in the case of the octanediol, probably due to the nonequivalence of its OH groups, of which the tertiary is eliminated at a lower temperature than the primary.

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CONTACT CONVERSIONS OF CYCLOOCTANE IN THE PRESENCE OF A NICKEL CATALYST

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Academician B. A. Kazanskii

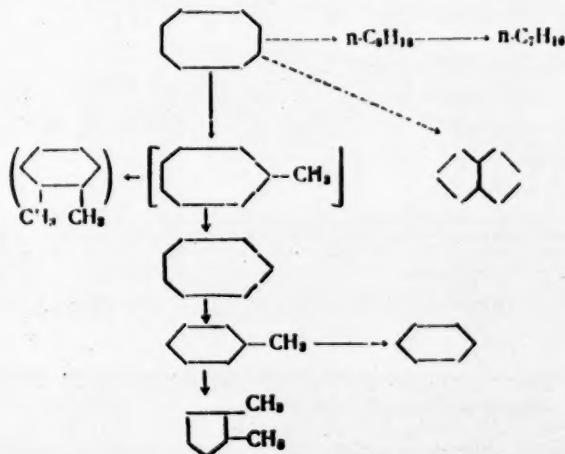
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February, 1961

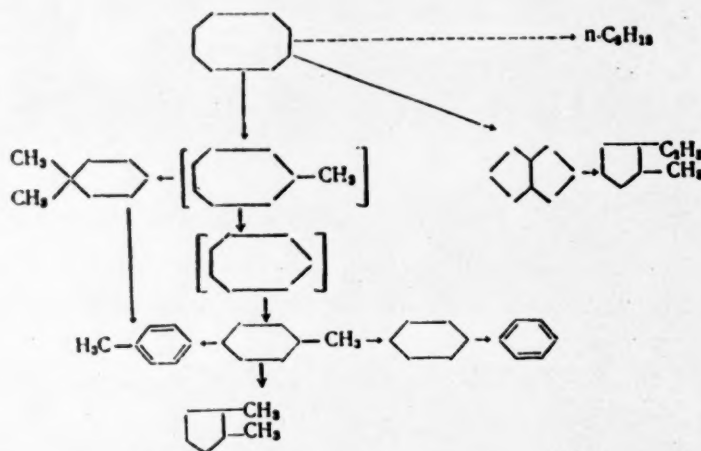
Original article submitted November 11, 1960

In 1908 Willstätter and Kametaka [1] attempted to study the conversions of cyclopentane and cyclooctane over nickel at 205-250°. Working with small amounts of material (2-3 g) and lacking refined investigation methods, the authors were unable to identify the reaction products. However, they put forward the hypothesis that passing cyclopentane vapor over nickel in a stream of hydrogen at 235° formed methylcyclohexane and at 250°, aromatic hydrocarbons. In their opinion, cyclooctane was isomerized at 205-210° mainly to dimethylcyclohexane, possibly with some alkylated cyclopentanes. The authors specifically stated that normal paraffins, namely n-heptane and n-octane, were not detected.

In the present work we investigated the conversions of cyclooctane over a nickel catalyst (50% nickel on kieselguhr) at 200 and 250° in a stream of hydrogen. The catalyzate obtained from cyclooctane at 200° was passed over the catalyst at the same temperature twice more. The conversion of cyclooctane was ~61%, while two catalytic treatments at 250° produced ~81% conversion of cyclooctane. The final catalyzates obtained were distilled on an efficient column, and the composition of the fractions was examined by Raman spectroscopy. The determinations showed that the catalyzates had the following composition: The catalyzate obtained at 200° consisted of n-octane (~15% of the weight of the liquid catalyzate), cycloheptane (~6%), cis-1,2-dimethylcyclopentane (~5%), n-heptane (~4%), methylcyclohexane (~3%), cyclohexane (less than 1%), and a very small amount of cis-bicyclo-(0,3,3)-octane (cis-pentalane). In addition, there were grounds for considering that the catalyzate contained trans-1,2-dimethylcyclohexane. About 46.5% of the weight of the catalyzate was unreacted cyclooctane. The data obtained indicate the following scheme for the reaction:



The catalyzate obtained at 250° consisted of cis-pentalane (~8% of the catalyzate weight), toluene (~11%), and benzene (~2%) in addition to unreacted cyclooctane. We also detected methylcyclohexane, cyclohexane, cis-1,2-dimethylcyclopentane, and gem-dimethylcyclohexane, whose quantitative proportions we were unable to determine. The data obtained indicate the following scheme for the conversion of cyclooctane over a nickel catalyst at 250°:



Thus, when cyclooctane was passed over nickel on kieselguhr in a strong stream of hydrogen at comparatively low temperatures (200-250°), three processes occurred: the hydrogenolysis of the eight-membered ring to form n-octane, which we detected for the first time and which is analogous to the hydrogenolysis of compounds with smaller rings [2-5]; transannular dehydrogenation, leading to cis-pentalane; and stepwise isomerization of cyclooctane to compounds with seven-, six-, and five-membered rings. The reaction temperature plays an important role in the quantitative ratio of these processes. Thus, hydrogenolysis of cyclooctane occurs to an appreciable extent only at 200°, while this process is hardly observed at 250°, and the formation of pentalane is mainly characteristic at 250°. Isomerizations of rings accompanied by hydrocracking occurs at both 200 and 250°, but at 250° they are also complicated further by aromatization of hexamethylene hydrocarbons. It is interesting to note that the cis-1,2-dimethylcyclopentane detected in the catalyzates is probably formed as a result of these isomerization processes. This is confirmed by the fact that the catalyzate obtained at 200° contained more of this hydrocarbon than the catalyzate obtained at 250°, as had the cis-1,2-dimethylcyclopentane been formed from cis-pentalane as a result of hydrogenolysis of cis-pentalane and hydrocracking of the 1-methyl-2-ethylcyclopentane thus formed, there would have been more cis-1,2-dimethylcyclopentane at 250°, as cis-pentalane is hardly formed at 200° and 1-methyl-2-ethylcyclopentane was not found in the catalyzate. The decrease in the amount of cis-1,2-dimethylcyclopentane when the reaction was carried out at 250° may be explained by the fact that in this case there are the competing processes of the conversion of methylcyclohexane to cis-1,2-dimethylcyclopentane on the one hand and aromatic hydrocarbons (benzene and toluene) on the other, and the equilibrium is displaced toward the formation of the latter. Aromatization processes do not occur at 200°, and therefore the percentage conversion of methylcyclohexane to cis-1,2-dimethylcyclopentane is greater at this temperature than at 250°.

It should also be noted that transannular dehydrogenation of cyclooctane to cis-pentalane and isomerization of hydrocarbons also occur in the presence of platinized charcoal, but at a higher temperature (310°) [6, 7]. Special experiments of ours showed that cyclooctane is unchanged when passed over active 5% platinized charcoal in a stream of hydrogen at 200 and 250°.

EXPERIMENTAL

The cyclooctane [7] used in the work had the following constants: b. p. 149.5° (745 mm), n_D^{20} 1.4588, d_4^{20} 0.8356. Literature data [8]: b. p. 150.7° (760 mm), n_D^{20} 1.45837, d_4^{20} 0.8362.

Contact conversions of cyclooctane at 200°. Into a quartz tube was placed 48 ml (41.2 g) of a nickel catalyst consisting of equal amounts of nickel and kieselguhr, and over this was passed 26 g of cyclooctane at a

TABLE 1

Fraction No.	Boiling range at 727 mm in °C	n_D^{20}	d_4^{20}	Aniline point	Amount	
					in g	in wt. %
1	93,7	1,3885	—	—	0,95	4,4
2	93,7—103	1,3970	0,7070	—	1,66	7,7
3	103—119	1,4211	0,7604	—	1,4	6,5
4	119—130	1,4095	0,7337	59,8	4,57	21,2
5	130—140	1,4431	0,8150	—	2,56	11,9
6	140—149	1,4581	0,8372	—	5,83	27,0
7	Residue	1,4587	0,8348	—	4,14	19,2
	Losses	—	—	—	0,45	2,0

TABLE 2

Hydrocarbons present in fractions	Fraction no.							Total in catalyzate	
	1+2	3	4	5	6	7		in g	in wt. %
	Hydrocarbon content, weight %								
n-Heptane	30	—	—	—	—	—		0,8	3,7
n-Octane	—	15	60	+	—	—		3,1	14,5
Cis-1,2-dimethylcyclopentane	40	—	—	—	—	—		1,0	4,6
Cyclohexane	5	—	—	—	—	—		0,13	0,6
Methylcyclohexane	15	15	—	—	—	—		0,6	2,8
Cycloheptane	—	35	15*	—	—	—		1,2	5,5
Cis-Pentalane	—	—	+	—	—	—			
Cyclooctane	—	—	—	—	Main content			10	46,5

* Hydrocarbon detected qualitatively.

TABLE 3

Fraction No.	Boiling range at 745 mm in °C	n_D^{20}	d_4^{20}	Amount	
				in g	in wt. %
1	up to 94	1,4110	0,7319	1,18	9,9
2	94—100	1,4010	0,7131	1,33	11,0
3	100—119	1,4585	0,8115	2,20	19,0
4	119—127	1,4112	0,7329	2,90	24,1
5	Residue	1,4594	0,8276	3,40	28,3
	Losses	—	—	0,99	8,3

space velocity of 0.28 in a strong stream of hydrogen at 200°. The catalyzate obtained was subjected to catalytic treatment twice more under the same conditions; this gave the following results:

Run	No. 1	No. 2	No. 3
Amount of catalyzate, g	24,1	22,3	21,56
n_D^{20}	1,4470	1,4370	1,4350

The total losses, including the gaseous hydrocarbons formed, were ~16% in the three catalytic treatments.

The catalyzate, which showed a negative formolite reaction (indicating the absence of aromatic and unsaturated hydrocarbons), was fractionated on a column of 40 theoretical plates. The results of the distillation are given in Table 1.

The compositions of all the fractions were established by examination of the Raman spectra (see Table 2).

The presence of lines at 500 and 749 cm^{-1} in the spectra of the third and fourth fractions indicated that these fractions contained trans-1,2-dimethylcyclohexane. In addition, strong lines were detected at 730 and 1002 cm^{-1} in the spectrum of the fifth fraction and these could not be interpreted.

Contact conversions of cyclooctane at 250°. The experiments were carried out under conditions analogous to those described above. An 18,4-g sample of cyclooctane was used. The catalyzate was passed over the catalyst again; the experimental results were as follows:

Run	No. 1	No. 2
Amount of catalyzate, g	13,4	12,0
n_D^{20}	1,4360	1,4320

The total losses, including the gaseous hydrocarbons formed, were ~34%.

The catalyzate was fractionated on a column of 40 theoretical plates. The results of the distillation are given in Table 3. The compositions of all the fractions were established by examination of the Raman spectra (see Table 4).

TABLE 4

Hydrocarbons present in fractions	Fraction No.				Total in catalyzate	
	1+2	3	4	5	in g	in wt. %
	hydrocarbon content, wt. %					
Benzene	10	—	—	—	0,25	7,1
Toluene	+	60	—	—	1,3	10,8
Cyclohexane	+	2	—	—		
Methylcyclohexane	+	3	—	—		
1,1-Dimethylcyclohexane	—	—	2	—	0,06	0,5
Cis-1,2-dimethylcyclopentane	+	7	—	—	0,2	1,7
Trans-1-methyl-2-ethylcyclopentane	—	—	+	—		
n-Octane	—	—	+	+		
Cis-pentalane	—	—	35	+	1,0	8,3
Cyclooctane	—	—	—	Main content	3,4	28,3

* Hydrocarbon detected qualitatively.

The procedure for obtaining and measuring the Raman spectra used in the present work was analogous to that described previously [7].

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SYNTHESIS OF NUCLEOTIDE COENZYMES AND RELATED COMPOUNDS

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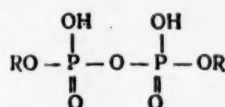
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(Presented by Academician A. N. Nesmeyanov, September 13, 1960)

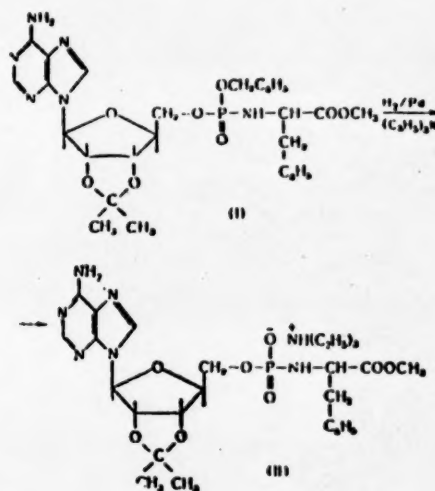
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Original article submitted September 7, 1960

In previous work [1] we demonstrated the possibility of using P-amino acid derivatives of nucleoside-5'-phosphate in the synthesis of nucleotide coenzymes of the ATP type. The study of this reaction is interesting in connection with the possibility of this process occurring in the cell, where activation of the phosphate residue of the nucleotide may be effected not simply by ammonia, but by amino acids or even proteins (enzyme systems). In attempting to synthesize unsymmetrical nucleotide coenzymes of the type



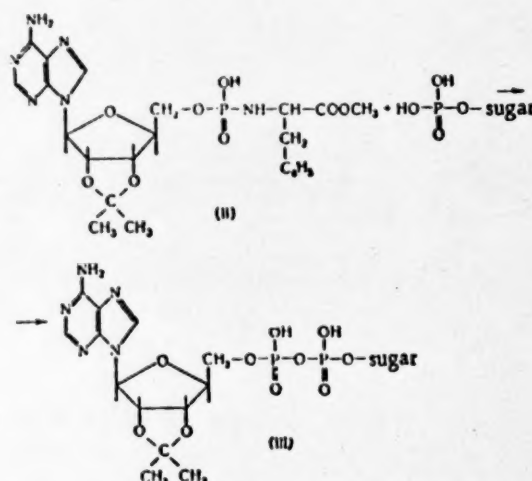
(where R is a nucleoside and R' a sugar residue), in the present work we studied the reaction between the methyl ester of N-(2': 3'-isopropylideneadenosine-5'-phospho)-phenylalanine (II) and ribose-5-phosphate or glucose-6-phosphate. The starting nucleoside-5'-phosphoamino acid (II) was prepared by hydrogenolysis of the methyl ester of N-(2': 3'-isopropylideneadenosine-5'-benzylphospho)-phenylalanine [1] in the presence of triethylamine.



It should be noted that the hydrogenolysis of I in the presence of triethylamine proceeded smoothly and gave a high yield of the triethylammonium salt of II, which is stable.* The free compound II was prepared from the

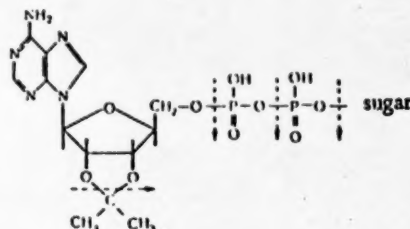
* In contrast to the extremely unstable free compound II [1].

salt (by addition of an equimolar amount of hydrogen chloride in dioxane) directly before its reaction with the pyridinium or tributylammonium salt of the sugar phosphate. The reaction was carried out in dry pyridine at room temperature over a period of 3 days.



where the sugar is ribose or glucose.

The formation of the 2':3'-isopropylideneadenosine-5'-diphosphosugar (Ip-ADP-sugar) (III) was demonstrated chromatographically. The yield of III, determined from the ultraviolet absorption [2], was 25-40%. The structure of III was established by its hydrolysis with 0.01 N HCl (100°, 10 min), which yielded adenosine, adenosine-5'-phosphate, adenosine-5'-diphosphate, and the sugar (ribose or glucose).



When the triethylammonium salt of the nucleotide coenzyme was used for the reaction instead of the free compound II, the synthesis was much slower. Dioxane could be used as the solvent in some cases instead of pyridine, but yield of Ip-ADP-glucose when the reaction was carried out in this solvent was much lower than in pyridine.

Thus, it was established that P-amino acid derivatives of adenosine-5'-phosphate are quite reactive and may participate in nucleotide coenzyme synthesis.

EXPERIMENTAL

Chromatographic solvent systems: I n-butanol saturated with water; II isopropanol - 1% (NH₄)₂SO₄ solution (2:1) [3]; III 96% ethanol - 0.5 M ammonium acetate (pH 3.5) (5:2) [4]; IV n-butanol-water-acetic acid (4:5:1).

Paper electrophoresis was carried out with the following buffers: I - 0.075 M ammonium acetate (pH 3.5); II - borate (pH 8.28).

Reagents for detection of sugars: reagent I - mixture of equal volumes of 0.1 N AgNO₃ and 5 N NH₄OH [5]; reagent II - mixture of 1 volume of 1 N aniline in butanol and 2 volumes of 2 N H₃PO₄ in butanol [6]. After being sprayed with these reagents, the chromatograms were heated for 10 min at 105°.

The yields of nucleotide coenzymes were determined by ultraviolet spectrophotometry [2].

1. Triethylammonium salt of II. To a solution of 100 mg of I [1] in 20 ml of ethanol was added 0.08 ml of dry triethylamine. The mixture was hydrogenolyzed [7] over 10 mg of palladium black for 40-50 min (room temperature and atmospheric pressure). The catalyst was removed by filtration, the filtrate evaporated in vacuum at 30°, and the residue dissolved in chloroform. The chloroform solution was poured into dry ligroin. The triethylammonium salt of II was isolated and reprecipitated again 2 or 3 times. The yield was 75 mg (70%) and the m. p. 92-94° (with decomp.); $R_f = 0.47$ in system I. The substance was dried for 24 hr over P_2O_5 in vacuum.

Found %: C 51.85; H 6.52; P 4.8; N 14.4. $C_{23}H_{29}O_8N_6P \cdot (C_2H_5)_3N \cdot H_2O$. Calculated %: C 52.00; H 6.90; P 4.65; N 14.7.

Substance	R_f values in systems		
	II	III	IV
Adenosine	0,74	0,74	0,37
Adenosine-5'-phosphate	0,41	0,54	
Adenosine-5'-diphosphate	0,22	0,32	
Ribose	0,62	0,71	0,24
Glucose	0,54	0,64	0,14

2. Tributylammonium salt of ribose-5-phosphate. To a suspension of 0.5 g ($1.3 \cdot 10^{-3}$ mole) of the barium salt of ribose-5-phosphate in 10 ml of water was added 5 g of KU-2 (H^+) and the mixture stirred for 5 min. The resin was removed by filtration and washed with water, 0.66 ml ($2.8 \cdot 10^{-3}$ mole) of tributylamine added to the combined filtrates, the mixture subjected to lyophilic drying, and the residue dissolved in absolute pyridine. The tributylammonium salt of glucose-6-phosphate was prepared analogously.

3. Tributylammonium phosphate and pyrophosphate.

To 0.44 g of a mixture of phosphoric and pyrophosphoric acids [8] was added 1 ml of dry tributylamine and the mixture evaporated in vacuum (60-70°). Absolute dioxane was added to the residue.

4. 2':3'-Isopropylideneadenosine-5'-diphosphoribose (ip-ADP-ribose). To a solution of 20 mg ($3.1 \cdot 10^{-5}$ mole) of the triethylammonium salt of II in 1 ml of absolute dioxane was added 0.03 ml of a 1.03 N solution of hydrogen chloride in absolute dioxane ($3.1 \cdot 10^{-5}$ mole of HCl). The precipitate was removed by filtration and to the filtrate was added $1.2 \cdot 10^{-4}$ mole of the tributylammonium salt of ribose-5-phosphate in dry pyridine. The mixture was left for 3 days at 20° with protection from atmospheric moisture and chromatographed with system III. We detected II ($R_f = 0.87$), 2':3'-isopropylideneadenosine-5'-phosphate ($R_f = 0.69$), and a spot of unknown composition ($R_f = 0.50$). The lowest spot was eluted, the eluate evaporated in vacuum, and 0.01 N HCl added. The solution was boiled for 10 min, cooled, and chromatographed with systems II, III, and IV. On examination in ultraviolet light and spraying with sugar reagents, the chromatograms showed AMP, ADP, adenosine, and ribose (see the table for the R_f values in systems II, III, and IV). The eluate of the ADP spot was subjected to electrophoresis in buffer II for 2 hr (7v/cm with cooling of the paper in carbon tetrachloride). The electrophoregram showed one spot, which moved at the same rate as a control sample of ADP. The yield of ip-ADP-ribose was 25% (determined spectrophotometrically after chromatography in system III).

5. 2':3'-Isopropylideneadenosine-5'-diphosphoglucose (ip-ADP-glucose). To $3.1 \cdot 10^{-5}$ mole of II, prepared as described above, was added $1.2 \cdot 10^{-2}$ mole of the tributylammonium salt of glucose-6-phosphate in dry pyridine. The mixture was left for 3 days at 20° with protection from atmospheric moisture and chromatographed with system III. Apart from II ($R_f = 0.87$) and ip-AMP ($R_f = 0.69$), the chromatogram showed a spot with $R_f = 0.47$. This spot was eluted, the eluate evaporated, the residue hydrolyzed as described above, and the products chromatographed with systems II, III, and IV. We detected adenosine, AMP, ADP, and glucose (see the table for R_f values). The yield of ip-ADP-glucose was 37%.

6. ip-ADP and ip-ATP. These were prepared analogously from II and the tributylammonium salts of phosphoric and pyrophosphoric acids in absolute dioxane. The reaction mixture was subjected to electrophoresis in buffer I for 2 hr (15 v/cm). In addition to II and ip-AMP, the electrophoregram showed ip-ADP and ip-ATP, which moved at the same rate as control samples of ADP and ATP. The yields of ip-ADP and ip-ATP were 39 and 27%, respectively.

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CATALYTIC HYDROGENATION OF ORGANIC OXIDES IN A FLOW SYSTEM AT A HIGH HYDROGEN PRESSURE

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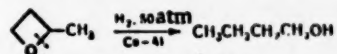
The catalytic hydrogenation of organic oxides may be of interest from two points of view: First, in this way it may be possible to establish the relative resistance of various oxide rings to opening by catalytically excited hydrogen; and second, in the hydrogenation of unsymmetrical organic oxides there is the problem of determining the direction in which opening of the oxide ring proceeds. Both these problems require a comparative study of the catalytic hydrogenation of various organic oxides. Available literature data are far from adequate for any general conclusions. As regards α -oxides, it is known that during the hydrogenation of monoalkyl- and monophenyl-substituted homologs on reduced nickel or copper, ring opening occurs at the bond connecting the oxygen atom to the carbon atom bearing the substituent, so that primary alcohols are formed [1].

Various β -epoxy-2-alkyl, 2,2-dialkyl, and 2-phenyl derivatives have been reduced with lithium aluminum hydride. It was established that in all cases the β -oxide ring is cleaved at the bond between the oxygen atom and the carbon atom bearing no substituents [2].

We recently investigated the hydrogenation of various γ -oxides (tetrahydrofuran homologs) in a flow system at normal pressure over platinized charcoal and a skeletal nickel-aluminum catalyst. Over platinized charcoal at 350°, tetrahydrofurans undergo hydrogenolysis at both C-O bonds simultaneously to form alkanes and water. Over a skeletal nickel-aluminum catalyst, 2-alkyl- and 2,2-dialkyltetrahydrofurans undergo hydrogenolysis at the C-O bond adjacent to the side alkyl groups, and the primary alcohols or aldehydes formed undergo further reactions to form alkanes whose carbon chain contains one carbon atom less than in the molecule of the starting tetrahydrofuran [3].

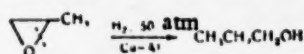
The purpose of the present investigation was to obtain systematic experimental material which could be used for comparative conclusions. We hydrogenated the simplest representatives of unsymmetrical α -, β -, and γ -oxides, namely propylene oxide, α -methyltrimethylene oxide, and α -methyltetrahydrofuran, in a flow system at a hydrogen pressure of 50 atm over two skeletal catalysts, Cu-Al and Ni-Al. α -Methyltrimethylene oxide was hydrogenated under these conditions over a skeletal Ni-Zn catalyst and α -n-propyltetrahydrofuran over a skeletal Ni-Al catalyst.

Hydrogenation of organic oxides over a skeletal Cu-Al catalyst. During hydrogenation over the skeletal Cu-Al catalyst at 190-200°, propylene oxide was converted into primary propyl alcohol in a yield of about 80%. This indicates that the α -oxide ring was opened at the C-O bond adjacent to the methyl group:

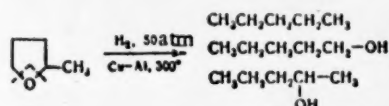


About 20% of the catalyzate consisted of a substance with a high boiling point.

Hydrogenation of α -methyltrimethylene oxide over the skeletal Cu-Al catalyst at 230-250° gave primary butyl alcohol in a yield of 90-95%. This indicates that the reaction proceeds in the following way:

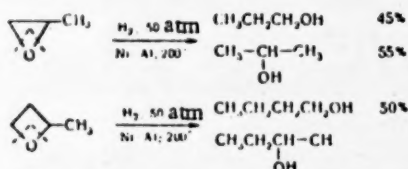


The degree of conversion of propylene oxide and α -methyltrimethylene oxide into propyl and butyl alcohols, respectively, was 80-95% under the above conditions. The tetrahydrofuran ring was found to be much more resistant to hydrogenolysis over a skeletal Cu-Al catalyst. Even at 300°, the conversion of α -methyltetrahydrofuran did not exceed 10%. Moreover, a sharp qualitative difference in the direction of opening of the γ -oxide ring as compared with α - and β -oxides was observed. The hydrogenolysis products of α -methyltetrahydrofuran (b. p. 79-79.5°, n_D^{20} 1.4060, d_4^{20} 0.8582) were n-pentane (30%),* 1-pentanol (35%), and 2-pentanol (35%). Thus, the hydrogenolysis of the tetrahydrofuran ring over skeletal Cu-Al proceeds in both possible directions:

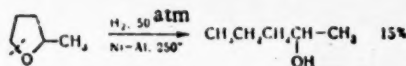


n-Pentane may be formed either as a result of the hydrogenolysis of the tetrahydrofuran ring simultaneously at both C-O bonds or as a result of the reduction of the amyl alcohols initially formed. The solution of this problem requires further investigation.

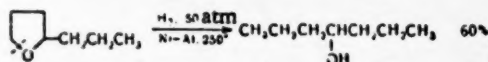
Hydrogenation of organic oxides on skeletal Ni-Al catalyst. In the hydrogenation of organic oxides, the skeletal Ni-Al catalyst shows properties which differ substantially from those of the skeletal Cu-Al catalyst. Propylene oxide and α -methyltrimethylene oxide, which underwent selective ring opening on skeletal Cu-Al, were cleaved in both directions on skeletal Ni-Al catalyst:



In exactly the same way, skeletal Cu-Al and skeletal Ni-Al showed different properties toward the γ -oxide ring. α -Methyltetrahydrofuran was converted to 2-pentanol alone over skeletal Ni-Al at 250°, and the degree of conversion was only about 15%. Thus, on this catalyst the γ -oxide ring undergoes hydrogenolysis by a different route to α - and β -oxides with the ring opened in only one direction, namely at the C-O bond remote from the side alkyl radical:



It is interesting to note that under the same conditions α -n-propyltetrahydrofuran (b. p. 131-132°, n_D^{20} 1.4232, d_4^{20} 0.8562) was converted into 4-heptanol (b. p. 153-155°, n_D^{20} 1.4710, d_4^{20} 0.8178) in a yield of ~60%, which evidently indicates that the length of the alkyl radical in the α -position has an effect on the resistance of the tetrahydrofuran ring to hydrogenolysis:

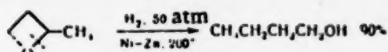


In connection with these results we should point out an experimental fact concerning the effect of pressure on the hydrogenolysis of the tetrahydrofuran ring.

* The yield given was calculated on the α -methyltetrahydrofuran converted.

In studying the hydrogenation of α -n-propyltetrahydrofuran over skeletal Ni-Al catalyst at normal pressure, we found previously that ring opening occurs in this case at the C-O bond adjacent to the side alkyl group [3]. These results show quite definitely that pressure has an effect on the direction of opening of an unsymmetrical γ -oxide ring.

In the present investigation we made another observation on the effect of the second component on the properties of skeletal nickel catalysts. It was found that during hydrogenation on skeletal Ni-Zn under conditions completely analogous to the conditions of hydrogenation on skeletal Ni-Al, α -methyltrimethylene oxide was converted only into primary butyl alcohol, i.e., in contrast to skeletal Ni-Al, skeletal Ni-Zn produced opening of the β -oxide ring in only one direction, i.e., at the C-O bond adjacent to the methyl group:



As we established previously [4], the difference in the properties of skeletal Ni-Al and skeletal Ni-Zn catalysts also appears in the hydrogenation of furan compounds.

To sum up, we may draw the following basic conclusions: During hydrogenation on skeletal Cu-Al and Ni-Al catalysts in a flow system under a high hydrogen pressure, α - and β -oxides behave analogously as regards the direction of opening of the oxide ring. On skeletal Cu-Al catalyst these oxides undergo ring opening was quite a high degree of selectivity at the C-O bond adjacent to the alkyl substituent, while on skeletal Ni-Al catalyst they undergo hydrogenolysis in both directions to approximately equal extent. On the other hand, unsymmetrical γ -oxides (α -alkyltetrahydrofurans) are hydrogenated selectively on a skeletal Ni-Al catalyst with opening of the ring at the C-O bond remote from the alkyl radical, and on a skeletal Cu-Al catalyst hydrogenolysis of γ -oxides proceeds in both directions.

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MOLECULAR COMPOUNDS OF DIPHENYLCYCLOPROPENONE,
TROPONE, AND BENZOPHENONE WITH HYDROGEN CHLORIDE

Yu. G. Borod'ko and Corresponding Member Academy
of Sciences of the USSR Ya. K. Syrkin

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February, 1961

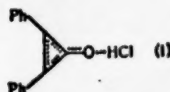
Original article submitted November 5, 1960

Using infrared absorption spectra, we studied the intermolecular reaction of ketones which have no enol form with HCl. As examples we used diphenylcyclopropenone (DPCP), tropone, and benzophenone. The first two substances are of interest as they contain seven- and three-membered rings which are readily converted into a cationic form and would seem to be capable of stronger interaction with HCl.

We plotted the infrared absorption spectra of DPCP in solutions of CCl_4 , C_2Cl_4 , CHCl_3 , and C_6H_6 , through which gaseous HCl was passed. The temperature range was from 10 to 60°. The HCl concentration in the solution was determined by titration. As Fig. 1 shows, when HCl was passed through a solution of DPCP in CHCl_3 , the intense absorption in the regions of 1845 cm^{-1} (corresponding to valence vibrations of the carbonyl group [1]) and 1623 cm^{-1} (valence vibrations of the $\text{C}=\text{C}$ bond in the cyclopropene ring) strongly decreased and a new, intense band appeared at about 1420 cm^{-1} .

There was a considerable increase in the intensity of absorption in the region of valence vibrations of C^{12}C and $\text{C}-\text{H}$ bonds of the phenyl rings, though the frequencies remained practically unchanged. Absorption appeared in the region of 2780 cm^{-1} and also another series of less intense bands, whose positions are given in the table. With a rise in temperature from 20 to 50° (Fig. 1), the intensity of the new bands decreased and the spectrum approached that of pure DPCP in chloroform (an analogous picture was observed in other solvents).

From the temperature dependence of the integral intensity of the carbonyl band (in the region of concentrations of $10^{-2} - 10^{-4}$ mole/liter) we estimated the enthalpy (ΔH), entropy (ΔS) and free energy (ΔF) of the formation of the molecular compound (I) and these were found to be as follows: $\Delta H = -6000$ cal/mole, $\Delta S = -14$ entropy units, and $\Delta F = -1840$ cal/mole. Experiments showed that ΔH , ΔS , and ΔF were independent of the nature of the solvents we used.



It is important that the spectrum did not show absorption in the region of valence vibrations of the OH group, while the absorption at about 2780 cm^{-1} indicates the presence in solution of undissociated but perturbed HCl molecules. In our opinion, the experimental data presented indicate that a hydrogen bond is formed between DPCP and HCl. Stronger interaction with the formation of an OH bond and the appearance of two ions apparently does not occur.

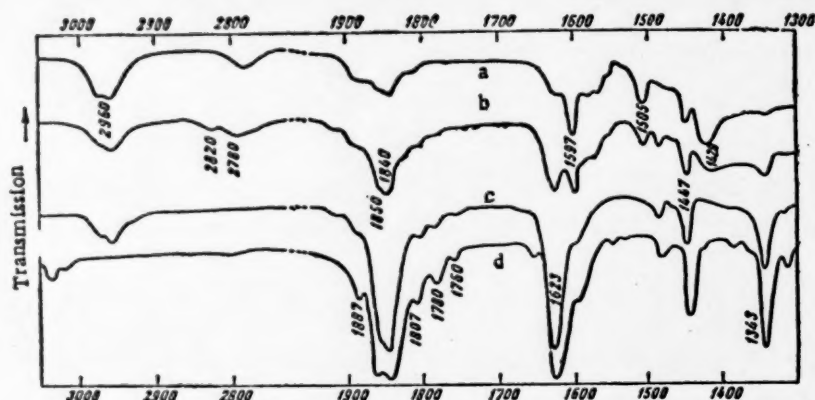


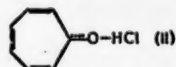
Fig. 1. Infrared absorption spectra: a) DPCP + HCl in CHCl_3 , $t = 20^\circ$; $C_{\text{DPCP}} = 6.6 \cdot 10^{-2}$ mole/liter; b) the same at $t = 52^\circ$; c) DPCP in chloroform, $t = 30^\circ$, $C_{\text{DPCP}} = 6.8 \cdot 10^{-2}$ mole/liter; d) DPCP pressed in KBr, $t = 30^\circ$.

Frequencies of Infrared Absorption Bands of DPCP, Troponone, and Molecular Compounds with HCl and HBr (cm^{-1})

DPCP pressed in KBr	DPCP in CHCl_3 , $C = 6.8 \cdot 10^{-2}$ mole/liter	DPCP + HCl in CHCl_3 , $C = 6.4 \cdot 10^{-2}$ mole/liter	DPCP + HBr, crystal.	Troponone	Troponone + HCl, crystal.	Troponone + HBr, crystal.
513				492	504	505
687				589	595	592
702				715	707	710
764				790	785	789
786				850	855	860
1023				908	938	944
1082				1025	960	985
1165				1221	1229	1230
1180				1260	1254	1251
1314				1315	1295	1285
1344	1343	1340		1416	1345	1335
1446	1447	1420*	1416	1478	1495	1410
1485	1485	1448	1452			1460
1594	1595	1483	1482			1492
		1505*	1511			
		1572*	1575			
1760	1760	1597	1598	1525	1510	1512
1780	1780	1620	1650	1590	1612	1618
1807	1807	1807		1640		
1840	1840	1840		1708		
1855	1850	1850				
1887	1887					
		2750*	2380		2790	2393
		2820			2950	
	2960	2960	2960	2997		2960
3030						

* Frequencies belonging to the molecular compound.

It should be noted that the molecular compound (II) is readily soluble in water and tetrahydrofuran, and spectra plotted in these solvents were found to be the same as that of pure troponone. This means that solution of the molecular compound in tetrahydrofuran, for example, leads to regeneration of pure troponone:



We were unable to measure ΔH of formation of this molecular compound as we were unable to find a suitable inert solvent.

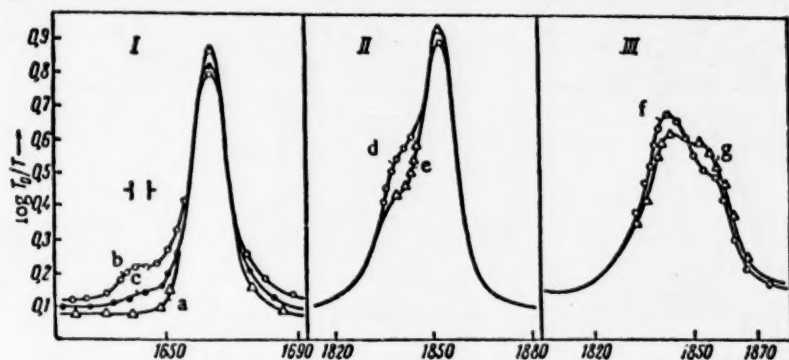


Fig. 2. Contours of carbonyl bands, I: a) benzophenone in C_2Cl_4 , $C_{BP} = 1.9 \cdot 10^{-3}$ mole/liter, $t = 30^\circ$; b) benzophenone + HCl in C_2Cl_4 , $C_{BP} = 1.9 \cdot 10^{-3}$ mole/liter, $C_{HCl} = 7 \cdot 10^{-2}$ mole/liter, $t = 25^\circ$; c) the same at $t = 55^\circ$. II: d) DPCP in CCl_4 , $C = 1.1 \cdot 10^{-3}$ mole/liter, $t = 10^\circ$; e) the same at $t = 55^\circ$. III: f) DPCP in $CHCl_3$, $C = 5 \cdot 10^{-4}$ mole/liter, $t = 10^\circ$; g) the same at $t = 55^\circ$.

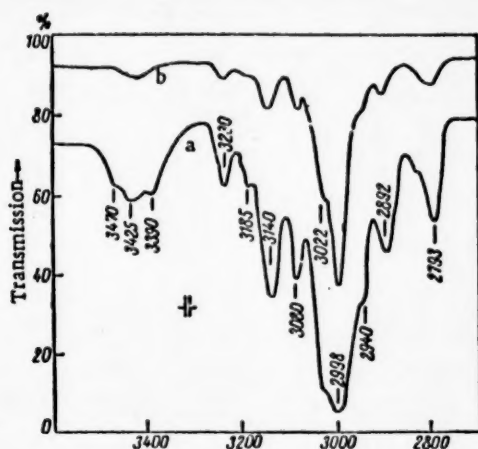
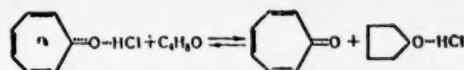
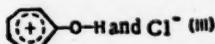


Fig. 3. Absorption of tropone in the region of $2700-3600\text{ cm}^{-1}$ in C_2Cl_4 solution: a) $C_{trop} = 0.27$ mole/liter; b) $C_{trop} = 4.6 \cdot 10^{-2}$ mole per liter.

carbonyl group vibrations of tropone and DPCP as a result of the formation of molecular compounds with HCl and HBr is remarkable. Such displacements of the frequencies are observed only in the formation of complexes of ketones with compounds of the type $AlCl_3$, $SnCl_4$, and $TiCl_4$ [4]. Thus, for example, in the complexes $AlCl_3$ -benzophenone $\nu_{C \cdots O} = 1515\text{ cm}^{-1}$, and acetone- $SnCl_4$ $\nu_{C \cdots O} = 1545\text{ cm}^{-1}$. The formation of a hydrogen bond between normal ketones and acetic, formic, and hydrohalic acids reduces the frequency of CO group vibrations by $15-30\text{ cm}^{-1}$.

In the case of diphenylcyclopropenone and tropone, the tendency to form the stable aromatic cyclopropenylum and tropylium systems leads to a very large reduction in the vibration frequencies, probably as a result of a decrease in the multiplicity of the $C \cdots O$ bond.

It should be noted that in a number of papers [3, 5] it was suggested that in the reaction of tropone and DPCP with gaseous HCl, HBr, and HI there are formed saltlike compounds containing the ions (III), for example



The enthalpy of formation of the complex $C_4H_8O \cdots HCl$ was $\sim 9-10$ kcal/mole (according to preliminary results obtained in our laboratory). The regeneration of tropone from compound (II) by the action of H_2O and C_4H_8O confirms that there is only a hydrogen bond between tropone and HCl. An analogous result was obtained in the case of DPCP. The frequencies in the infrared spectra of the crystalline compounds of DPCP and tropone with HBr are given in the table. Molecular compounds were also formed in this case.

No appreciable changes occurred in the spectrum of benzophenone when a solution of the latter was saturated with gaseous HCl. There was only a change in the contour of the band corresponding to the carbonyl bond with a frequency of 1664 cm^{-1} , and near to this there appeared a peak with the frequency of 1642 cm^{-1} (Fig. 2), which belonged to vibrations of the $C=O$ group, perturbed by the formation of a weak hydrogen bond. The large fall in the frequency of the

The absence from the infrared spectrum of absorption in the region of valence vibrations of the OH group, the presence of a band with the frequency 2780 cm^{-1} , which belongs to undissociated HCl molecules, the low enthalpy of reaction ($\Delta H = -6000\text{ cal/mole}$), which is characteristic of the reaction of ketones and ethers with HCl [6], and the regeneration of ketones under the action of water and tetrahydrofuran show, in our opinion, that the reaction is limited to the formation of a hydrogen bond alone. This is also supported by the temperature reversibility as the salt (III) would not be decomposed so readily with a slight rise in temperature.

There is a report in the literature [7] that tropone absorbs in the region of 3425 cm^{-1} , and this compelled us to study this section of the spectrum, as according to its structure tropone should not have basic vibration frequencies in the region of valence vibrations of OH and NH bonds. Experiments showed that there is actually absorption in this region (Fig. 3), but its intensity is two orders less than the bands belonging to the basic vibrations.

We therefore consider that the absorption at about 3425 cm^{-1} is a second-order line.

We should also note that the contour of the carbonyl band of DPCP is double and the change in it in relation to solvent and temperature (Fig. 2) is analogous to that observed previously [1] for the carbonyl band of syndones. We will consider the nature of the splitting in a separate communication.

We would like to thank Corresponding Member Acad. Sci. USSR D. N. Kursanov, who allowed us to synthesize tropone in the laboratory he directs, M. I. Vol'pin for providing a diphenylcyclopropenone preparation, N. G. Uvarova for helping with the experimental work and I. Yu. Kokoreva for synthesizing the tropone.

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DETERMINATION OF THE HEAT OF FORMATION OF INDIUM ANTIMONIDE BY FUSION IN A CALORIMETER BOMB

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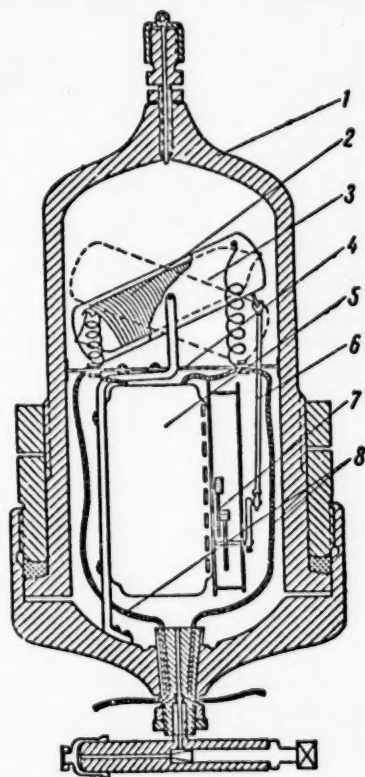
(Presented by Academician V. N. Kondrat'ev, October 6, 1960)

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February, 1961

Original article submitted October 5, 1960

Existing methods for determining heats of formation are not always applicable to semiconductor materials (combustion and solution) or are laborious (metal calorimetry) and some are of low accuracy (emf, vapor pressure, etc.).



1) Calorimeter bomb; 2) quartz ampoule-furnace; 3) furnace jacket; 4) silver shield; 5) electric motor; 6) crank gear; 7) reducing gear; 8) current leads.

The purpose of the present investigation was to develop a new method for determining the heat of formation of binary semiconductor compounds. The experiments were carried out on a calorimetric apparatus with an isothermal jacket [1]. In the bomb, which was of the type used in the thermal laboratory of Moscow University, was fixed a small electric furnace (see figure), which consisted of a quartz ampoule, 11 mm in diameter and 4 mm long. Onto the ampoule was wound a heating element, which consisted of a nichrome wire, 0.15 mm in diameter, with a resistance of 110 ohm. To prevent the wire turns from slipping during heating, they were covered with a thin layer of a pasty mixture of kaolin, borax, and water, which was dried at the synthesis temperature. A current of about 1 amp at a voltage of 120 v was fed to the furnace through a voltage stabilizer. The work of the current was measured with a highly accurate ac meter (produced by the "Étoalon" factory). The temperature change of the calorimeter was measured with a MMT-4 thermistor.

Into the bomb was fixed an electric motor with reducing gear and a crank gear for mixing the molten mixture by rocking the ampoule; the rate was 10 rocks per minute. The motor was connected in parallel with the furnace and consequently there was mixing only during heating.

The thermal value of the calorimeter, which equalled $2904 \pm 0.6 \text{ cal}_{15}$, was determined on benzoic acid with the introduction of appropriate corrections for the equipment introduced into the bomb (motor, furnace, etc.) which was absent during the combustion of benzoic acid. The electrical energy meter was then graduated by heating the empty ampoule in the bomb; one rotation of the meter needle corresponded to $41.40 \pm 0.02 \text{ cal}$.

Both an empty and a filled ampoule were heated for 4 min (meter reading, 150 rotations). Thereupon, about 6000 cal were

liberated and the rise in temperature of the calorimeter was 2,15° with an empty and 2,30° with a filled ampoule. Consequently, the heat effect of the reaction was responsible for a temperature rise of 0,15°, and therefore the experiments had to be carried out very carefully to obtain sufficiently accurate results.

In separate experiments it was established that the temperature inside the furnace reached 700° 50 sec after the current had been switched on. A silver screen, whose edge was firmly fixed to the walls of the bomb, was arranged between the electric motor and the furnace. The shield protected the motor from the heat of the furnace, reflecting and conducting it to the walls of the bomb. Due to this, the main period of the experiment was shortened by 6-7 min. The bomb was filled with nitrogen at 30 atm. This, in its turn, shortened the main period by a further 8-9 min and thus reduced it to 15 min (30 readings). For checking the reliability of the procedure we used indium antimonide, which had been studied comparatively thoroughly.

Into the ampoule-furnace we placed 12 g of a stoichiometric mixture of indium and antimony (purity 99,999 and 99,992, respectively). After being pumped out to 10^{-3} mm Hg, the ampoule was sealed. To prevent fusion of the contents of the ampoule during sealing, the latter was cooled with a fine stream of water, which flowed close to the sealing point. The ampoule was then dried in air and fixed in a metal (tantalum) jacket, connected to the rocker rod.

Onto the furnace leads, which consisted of platinum wire 0,25 mm in cross section, were placed small pieces of glass capillary for electrical insulation. The degree of conversion was checked by x-ray diffraction and by chemical analysis.

TABLE 1

Expt. No.	Amount of substance reacting, g		Number of rotations of needle of electric meter	ΔT corrected	Q, cal		$-\Delta H_{298}^0$
	In	Sb			total	due to reaction	
1	5,8262	6,1816	150,25	2,2734	6605,20	385,55	3,78
2	5,8273	6,1827	150,06	2,2778	6615,46	403,55	3,97
3	5,8274	6,1828	150,70	2,2846	6635,46	397,05	3,91

TABLE 2

Expt. No.	$-\Delta H_{720}$, kcal/g-at	$-\Delta H_{720}$, kcal/g-at	$-\Delta H_{298}$, kcal/g-at	Determination method	Source
1	4,30	—	4,00	Tin calorim.	(3)
2	—	3,47	3,49	Tin calorim.	(4)
3	—	—	3,4	Direct fusion	(5)
4	3,98	—	3,67	Emf	(6)
5	—	—	3,89	Fusion in bomb	Present Investigation

Indium and antimony form one compound, InSb [2]. X-ray analysis* of the reaction products showed the presence of only cubic InSb. Lines belonging to individual components and the hexagonal modification of the substance were not detected. The products were analyzed chemically by treatment with 12 N hydrochloric acid saturated with hydrogen sulfide [5], which dissolves only free indium. It was thus found that there was 96-100% addition.

Table 1 gives the results of the experiments.

Thus, the standard heat of formation of indium antimonide $\Delta H_{298}^0 \text{ InSb}_{\text{cub}} = -3.89 \pm 0.04 \text{ kcal/g-at}$.

* The x-ray analysis was carried out by K. P. Mamedov and Z. D. Nurieva.

In Table 2 are the results of the present work and literature data for InSb.

As Table 2 shows, our results agree well with the data of other authors. ΔH of InSb is small and in this compound is closer to alloys than saltlike compounds. Higher accuracy can obviously be attained for compounds with comparatively high values of ΔH .

The given procedure can evidently be applied to multicomponent systems.

It should also be noted that the counterpressure of nitrogen in the bomb may prevent explosions which often arise during the synthesis of compounds whose components have a high vapor pressure.

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SYNTHESIS AND PROPERTIES OF POLYACETYLENE

Corresponding Member Academy of Sciences of the USSR

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Kudryavtsev, and K. Usenbaev

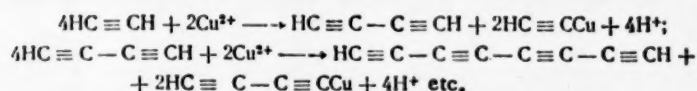
Institute of Mineral Fuels, Academy of Sciences of the USSR and Institute of
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Original article submitted November 4, 1960

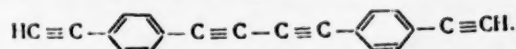
The oxidation of acetylides is known to yield bis-acetylenes [1]. It has also been reported [2] that in the oxidation of acetylides from bis-acetylenes of the type $\text{HC} \equiv \text{C} - (\text{CH}_2)_n - \text{C} \equiv \text{CH}$, together with cyclic diynes, there is also formed a small amount of products which have not been studied.

It may be considered that in the preparation of copper acetylide from acetylene and cupric salts the following reactions occur:



With excess copper ions the reaction will yield a mixture of polyynes and copper acetylides. Oxidation of the reaction mixture evidently leads to polyynes with the structure $\text{H} - (\text{C} \equiv \text{C})_n - \text{H}$.

The proposed mechanism for the formation of polyacetylene is demonstrated by the oxidation of the acetylide of p-dieethynylbenzene, which we described previously [3] and as a result of which we isolated and identified the dimerization product p,p'-dieethynyl-(diphenyl)-butadiyne.



We prepared the acetylide by passing acetylene into ammonia solution of a cupric salt. The oxidation was carried out with an aqueous solution of potassium ferricyanide at the boiling point of the mixture. The reaction yielded a black, insoluble powder, which contained 98% of C according to elementary analysis data. The product obtained was probably a mixture of polymer homologs of polyacetylene. In actual fact, heating the product in high vacuum yielded a small amount of a benzene-soluble crystalline substance, which gave a derivative characteristic of acetylenes with an ammonia solution of cuprous copper.

The curve given in Fig. 1 for the loss in weight of one polyacetylene sample in relation to treatment temperature (heating rate $8^\circ/\text{min}$) on a dynamometer with a quartz spring in a stream of purified nitrogen also shows that relatively low-molecular volatile products were present. The electron paramagnetic resonance spectrum of the substance obtained showed a narrow intense band characteristic of conjugated systems (the concentration of unpaired electrons per gram of substance was about 10^{18}) and the presence of chemically bound copper. These data indicate that the product obtained was a cumulene polymer which apparently had the structure $\text{H} - (\text{C} = \text{C} = \text{C})_n - \text{H}$ and contained a certain amount of copper.

An x-ray diffraction pattern of the polyacetylene, which was obtained by oxidation of copper acetylide with potassium ferricyanide and demineralized by brief treatment with hydrochloric acid, contained, in addition to a halo, a strong interference band corresponding to the period $d = 3.85 \text{ \AA}$, which may be assigned to the intermolecular distance in an ordered system of parallel, linear $(=C=C=)_n$ molecules.

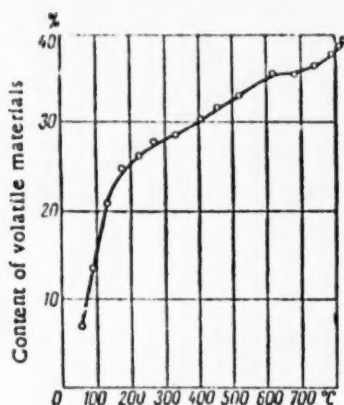


Fig. 1. Curve of weight loss of polyacetylene in relation to temperature.

The copper content of the polyacetylene obtained by oxidation with potassium ferricyanide was indicated by the formation of crystalline copper during high-temperature treatment and this was clearly shown on the x-ray diffraction patterns (Fig. 2e).

The high-temperature treatment at various temperatures was done under isothermal conditions ($\pm 25^\circ$) in a resistance furnace with a graphite heater in a stream of nitrogen. The samples were placed in a closed graphite crucible. During the high-temperature treatment, the carbon remained in the form of polyacetylene and no coke formation or graphitization was observed. Only treatment at 2300° led to graphite formation (Fig. 2h), which indicates the high thermal stability of polyacetylene.

After demineralization of the starting polymer with concentrated hydrochloric acid, the x-ray diffraction pattern showed only an intense halo (Fig. 2a), which is characteristic of the liquid type of molecular ordering. The same type of x-ray diffraction pattern showing a halo was obtained for samples of polyacetylene synthesized with the aid of a stronger oxidant (Fig. 2b).

The x-ray diffraction patterns showed the extremely interesting phenomenon of graphite formation during prolonged boiling of fired polyacetylene samples in concentrated hydrochloric acid (Fig. 2c,d,f,g). In contrast to polyacetylene with molecules in the form of linear chains of carbon atoms, the basic structure of elementary carbon and graphite is a monolayer of atoms of the trigonal valence modification. The ease of the rearrangement of the atomic chains of carbon into graphite monolayers with the corresponding transformation of the valence forms during treatment with hydrochloric acid seems strange.

Figure 3 gives the results of measuring the specific electrical resistance ρ of a polyacetylene sample obtained by oxidation with potassium ferricyanide in relation to treatment temperature (in a stream of nitrogen). The measurements were made by the null method with an MTV bridge. All the values given for the electrical resistance of powders were determined under a pressure of 50 kg/cm^2 . For the starting sample $\rho \sim 10^6 \text{ ohm} \cdot \text{cm}$. The decrease in ρ with a rise in temperature must be the result of the accumulation of crystalline copper due to thermal dissociation and liberation of the terminal copper atoms from polyacetylene. However, the specific electrical resistance continued to decrease at a higher temperature (above 2000°) when the copper evaporated from the polymer, and there was still no graphite formation. This indicates an increase in the length of the polyacetylene chains during pyrogenic synthesis due to thermal dissociation and liberation of copper with subsequent recombination of the free polymer radicals formed.

Figure 3 also gives the results of measuring the thermal emf (with respect to copper) of the same products from thermal treatment.

The thermal emf was measured by a compensation method with the aid of a PPTV high-ohm potentiometer. A mirror galvanometer with an internal resistance $R_{in} = 50 \text{ ohm}$ was used as a null instrument. The temperature of the sample-electrode contacts was measured with two chromel-alumel thermocouples. The original sample showed a very high negative thermal emf ($\alpha = 1.38 \cdot 10^4 \text{ } \mu\text{V/deg}$). At 1300 and 1500° α was found to be close to zero. With an increase in temperature above 1500° , α had a positive sign, and the temperature dependence gave a peculiar curve with a maximum at 2300° , which corresponds to the temperature of the transition of polyacetylene into graphite.

The results of investigating ρ and α of polyacetylene obtained by oxidation with potassium ferricyanide indicate that the starting sample studied was an n-type semiconductor in which the role of the electron donor was played by copper atoms incorporated in the carbon molecular chains with double bonds with a polyallene

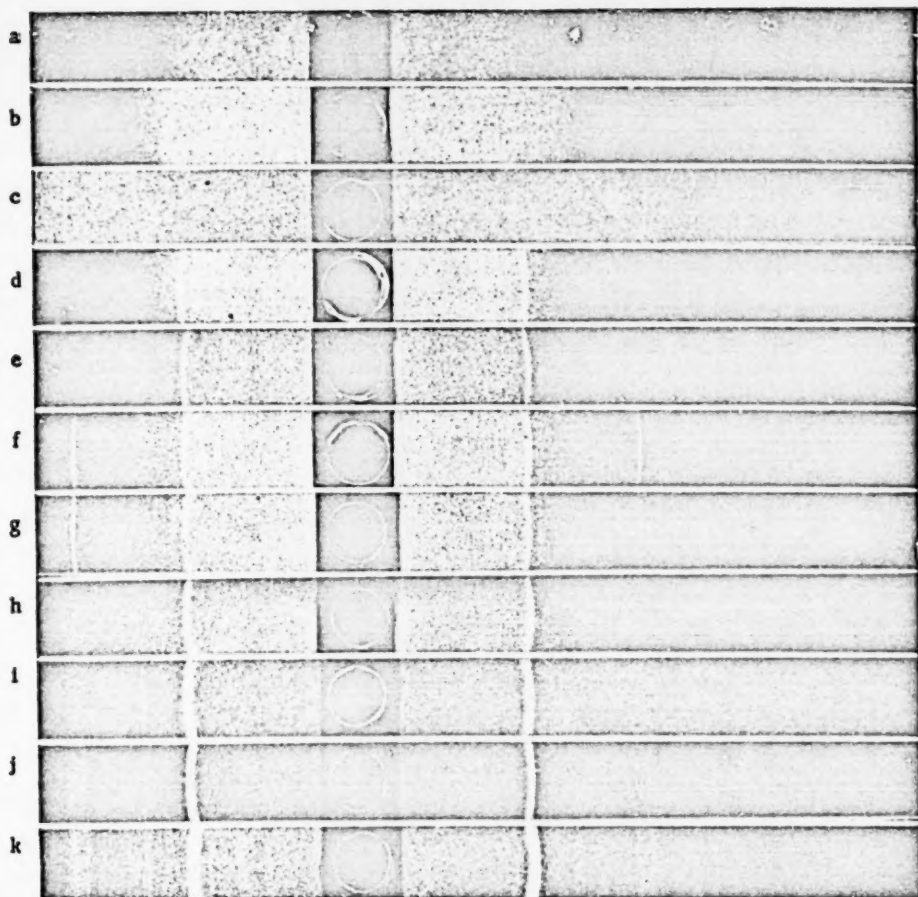


Fig. 2. X-ray diffraction patterns of polyacetylene and its thermal treatment products: a) original material after prolonged treatment with HCl; b) obtained with a strong oxidant; c) fired at 1800°; d) fired at 1300° and treated with HCl; e) at 1500° and treated with HCl; f) at 1800° and treated with HCl; g) at 2000° and treated with HCl; h) at 2300°; i) at 2500°; j) at 2800°; k) fired at 3000°. The duration of the isothermal treatment at the given temperature was 15 min.

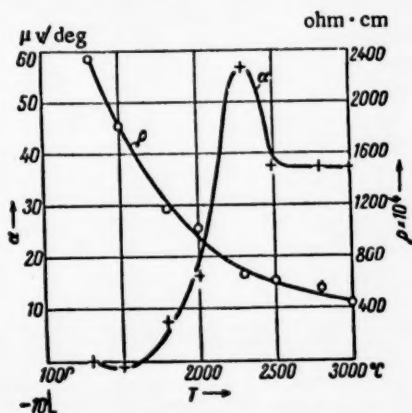


Fig. 3. Specific electrical resistance ρ and thermal emf α of the products from thermal treatment of polyacetylene.

structure. For polyacetylene samples obtained with stronger oxidants, namely nitrate ion or hydrogen peroxide, and not containing copper, the thermal emf was found to equal zero. This confirms that the residual copper atoms acted as the donor. The observed change in the sign of the thermal emf during thermal treatment corresponds to the change of the polyacetylene samples studied into a p-type semiconductor with hole positive charge carriers. This change is accompanied by thermal dissociation and elimination of copper and hydrogen atoms from the carbon chain and is apparently connected with the acceptor properties of the terminal carbon atoms.

The smooth nature of the change in ρ and α with a rise in temperature with a constant heating time is connected with the temperature dependence of the rates of thermal dissociation and recombination during the pyrogenic synthesis. As a result, there is elimination of copper and also hydrogen and an increase in the length of the carbon chains of polyacetylene.

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ISOTOPIC EXCHANGE OF HYDROGEN IN PRIMARY AND SECONDARY ALKYL CHLORIDES

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In our previous communications [1] it was shown that tertiary alkyl halides are capable of exchanging hydrogen atoms for deuterium in acid media with a high ionizing capacity, namely anhydrous formic acid and concentrated hydrochloric and hydriodic acids.

In media with a low ionizing capacity [2] such as anhydrous acetic acid, hydrogen exchange of tertiary alkyl halides does not occur without a catalyst, though it may be produced by catalytic amounts of aprotic acids such as FeCl_3 , SbCl_5 , ZnCl_2 , etc. These data led us to the concept that hydrogen exchange of tertiary alkyl halides is the result of heterolysis of the bond $\text{C}-\text{Hal}$ with the formation of carbonium ions, which are capable of exchange. On this basis one might expect that isotopic exchange of hydrogen in primary and secondary alkyl halides could also be produced if conditions are found under which the carbon-halogen bond is ionized.

Assuming that heterolysis of the carbon-halogen bond is a characteristic stage of the Friedel-Crafts reaction [3], we decided to study hydrogen exchange of primary and secondary alkyl chlorides under the action of aprotic acids of the type used for the Friedel-Crafts reaction in nitrobenzene. The deuterium donor in these reactions was deuterium chloride, whose solubility in nitrobenzene at room temperature is $\sim 2\%$.

Special experiments showed that nitrobenzene does not undergo hydrogen exchange with deuterium chloride under the conditions used, while the rate of hydrogen exchange of nitrobenzene in the presence of aprotic acids is very low (see section 3 of the experimental part). These observations made it possible for us to investigate hydrogen exchange of alkyl chlorides with deuterium chloride in nitrobenzene. It was found that there was no hydrogen exchange of primary and secondary alkyl chlorides in the absence of aprotic acids. However, in the presence of the aprotic acids AlCl_3 , FeCl_3 , SbCl_5 , and BF_3 there was rapid exchange of hydrogen atoms in both primary and secondary alkyl chlorides (Table 1).

To establish the relative activity of the different aprotic acids in nitrobenzene, we studied the rate of hydrogen exchange of isopropyl chloride in the presence of the same molar amounts of aprotic acids. The results of the kinetic experiments are given in Table 2. It was found that antimony pentachloride showed the highest activity in the hydrogen exchange of isopropyl chloride and stannic chloride the lowest among the aprotic acids listed. Mercuric chloride was unable to initiate hydrogen exchange.

The relative activity of the aprotic acids may be represented by the following numerical values:

SbCl_5	FeCl_3	AlCl_3	BF_3	SnCl_4
440	220	75	1	$\ll 1$

TABLE 1

Hydrogen Exchange of Alkyl Chlorides with DCl in Nitrobenzene in the Presence of Aprotic Acids at 25°. (Molar ratios of RCl: nitrobenzene: DCl = 1: 5-8; 0.2-0.3)

Expt. No.	RCl	MeHal _x	MeHal _x mole %	Time, min	EDWC,* γ/ml		
					calculated for α-H	found	
1	n-C ₄ H ₉ Cl The same	Without catalyst		100%	1900	70	
		FeCl ₃	3		20	1500	1450
		AlCl ₃	5		20	2150	580
		SbCl ₅	2		12	1600	1300
2	Sec-C ₄ H ₉ Cl The same	FeCl ₃	3	13	2240	1860*	
		AlCl ₃	10	32	1450	1380	
		SbCl ₅	6	31	1390	1240	
		BCl ₃	9	37	1310	660	
3	Tert-C ₄ H ₉ Cl The same	Without catalyst		5570	2700	610	
		FeCl ₃	3		13	2600	2650*
		AlCl ₃	3		10	2400	2370*
		Without catalyst			5320	2460	70
4	Iso-C ₄ H ₉ Cl The same	FeCl ₃	10	70		2370	2480
		AlCl ₃	9	63	2570	1450	

* Here and elsewhere in the article EDWC stands for the excess density of water from combustion.

** Experiments at 10°.

TABLE 2

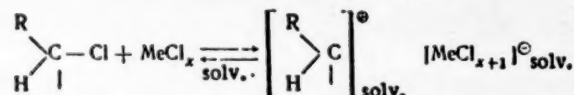
Hydrogen Exchange of Isopropyl Chloride with DCl in Nitrobenzene in the Presence of Aprotic Acids at 15°. (Molar ratio of Iso-C₃H₇Cl: nitrobenzene: DCl = 1: 8; 0.2-0.3)

Expt. No.	MeHal _x	Hydrogen exchange rate constant, K _{H.E.} · 10 ⁶ sec ⁻¹
1	Without catalyst	No exchange
2	SbCl ₅	880
3	FeCl ₃	440
4	AlCl ₃	150
5	BF ₃	2
6	SnCl ₄	2 (at 25°)
7	HgCl ₂	No exchange

It is interesting to note that our data on the activity of the aprotic acids agrees well with recently published data of Cotter and Evans [4], who investigated the effect of Friedel-Crafts catalysts on the ionization of triaryl-methyl chlorides in acetic acid. According to the data of these authors, the ionizing strength of the metal halides decreases in the following series:



The high lability of hydrogen atoms of primary and secondary alkyl halides in the presence of SbCl₅, FeCl₃, and AlCl₃ in nitrobenzene which we found agrees well with the hypothesis that strong aprotic acids in a medium with a high ionizing capacity may produce heterolysis of the carbon-chlorine bond in aliphatic chlorides, and hydrogen exchange in these cases is caused by the formation of carbonium ions in accordance with the scheme:



EXPERIMENTAL*

1. Starting materials. Alkyl chlorides. Secondary butyl chloride (b. p. 67.5-67.8°, n_D²⁰ 1.3949, d₄²⁰ 0.8726) was prepared from sec-butanol and thionyl chloride [5] and purified by distillation on a column with an efficiency of 30 theoretical plates. Tertiary butyl chloride with b. p. 51°, n_D²⁰ 1.3852, d₄²⁰ 0.8439 was obtained from tert-butanol by treatment with HCl and distilled on a column of 16 theoretical plates. n-Butyl

* A. N. Astakhova helped in the experiments.

chloride (b. p. 77-78°, n_D^{20} 1.4018, d_4^{20} 0.8858) and isopropyl chloride (b. p. 34.5-35°, n_D^{20} 1.3771, d_4^{20} 0.8592) were obtained from commercial products by distillation on a column with an efficiency of 30 theoretical plates.

Nitrobenzene. Commercial nitrobenzene was dried over phosphorus pentoxide and vacuum distilled (b. p. 85-86° at 10 mm, n_D^{20} 1.5524, d_4^{20} 1.2032). The dry nitrobenzene was saturated with deuterium chloride, and the concentration at room temperature was ~2%.

Aprotic acids. In our investigations we used commercial, chemically pure metal chlorides, $FeCl_3$, $SbCl_5$, $SnCl_4$, $AlCl_3$, and $HgCl_2$. The aluminum chloride, stannic chloride, and antimony pentachloride were further purified by vacuum sublimation in a nitrogen atmosphere. The ferric chloride and mercuric chloride were not purified further. The boron trifluoride, which was prepared by Meerwein and Panwitz method, was absorbed in dry nitrobenzene and added to the reaction mixture in this form.

TABLE 3

Sample No.	Time, min	EDWC of chloride, γ/ml		$K \cdot 10^4, sec^{-1}$
		calculated for $\alpha-H$	found	
1	10	2020	842	8.97
2	15	2020	1100	8.84
3	20	2020	1158	7.08
4	1263	2020	2180	

2. Experiments on hydrogen exchange of alkyl chlorides.*

Samples of aprotic acids were dissolved in nitrobenzene in an atmosphere of dry nitrogen in a special chamber. The alkyl chlorides were added to the reaction mixture and the samples removed also in a nitrogen atmosphere. The alkyl chlorides were isolated from the samples by vacuum distillation. In the case of fast reactions, the hydrogen exchange was stopped by pouring the samples into iced water. The liberated chlorides were washed with iced water and potassium carbonate solution, dried with calcium chloride, and distilled. As the kinetic experiments were carried out under similar conditions, we will describe only one experiment.

Hydrogen exchange of isopropyl chloride with DCl in nitrobenzene in the presence of $SbCl_5$. A 1.03-g sample (3.4 mmole) of $SbCl_5$ was dissolved in 44.52 g (362 mmole) of dry nitrobenzene. To the solution obtained was added 9.0 g (114.7 mmole) of isopropyl chloride in 67.88 g (54.6 mmole) of nitrobenzene containing 0.75 g (20 mmole) of deuterium chloride (86200 γ/ml). The solution was placed in a thermostat at 15°. Samples (25-30 ml) were taken from the reaction medium at definite time intervals; the isopropyl chloride was isolated from them by vacuum distillation and purified in the usual way. The results are given in Table 3.

3. Hydrogen exchange of nitrobenzene. Dry nitrobenzene was saturated with deuterium chloride, whose concentration was determined by titration with alkali in the presence of phenolphthalein. The deuterium content was determined from the excess density of water obtained by combustion of this solution. Nitrobenzene samples were washed with alkali, dried with P_2O_5 , distilled, and the deuterium content of the nitrobenzene determined by the usual method. The hydrogen exchange of nitrobenzene with DCl in the presence of aprotic acids was determined analogously (Table 4).

TABLE 4

Hydrogen Exchange of Nitrobenzene with DCl at 25-28°

Sample No.	MeHal _x	Molar ratios			Time min	EDWC, γ/ml	
		MeHal _x	DCl	nitrobenzene		calculated for meta-H	found
1	O	0	1.5	53	20000	580	0
2	$FeCl_3$	1	1.5	53	20000	580	160
					60500	580	470
3	$AlCl_3$	1	1.6	43	20000	580	160
					60500	580	410

Thus, it was established that primary and secondary alkyl chlorides undergo rapid hydrogen exchange with DCl in nitrobenzene in the presence of the strong aprotic acids $SbCl_5$, $FeCl_3$, and $AlCl_3$. The hydrogen exchange proceeds at a much lower rate in the presence of BF_3 and $SnCl_4$. Mercuric chloride does not initiate

* The isotopic analysis was carried out by N. V. Kislyakova and N. F. Mironova.

hydrogen exchange of primary and secondary alkyl chlorides under the same conditions. The data obtained confirm that hydrogen exchange of alkyl chlorides is caused by heterolysis of the carbon-chlorine bond and the formation of carbonium ions.

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ADDITION OF ISOPROPANOL TO MALEIC ACID INITIATED BY PERCARBONATES

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February, 1960

Original article submitted November 22, 1960

Plitts et al. [1] recently showed that the radicals obtained by abstraction of hydrogen from isopropanol by benzophenone during irradiation readily add to maleic acid to give terebic acid. We decided to carry out the addition of isopropanol to maleic acid with percarbonates as initiators. It was considered that in this way it might be possible to obtain additional data on the mechanism of percarbonate decomposition.

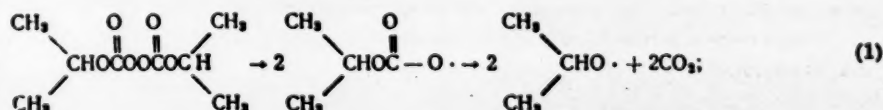
It was found that in the presence of dicyclohexyl and diisopropyl peroxydicarbonates at 50°, maleic acid reacts with isopropanol to give a high yield of terebic acid. We used about 0.1 mole of percarbonate per mole of maleic acid. The use of C¹⁴-labeled compounds made it possible to draw conclusions on the mechanism of the processes occurring.

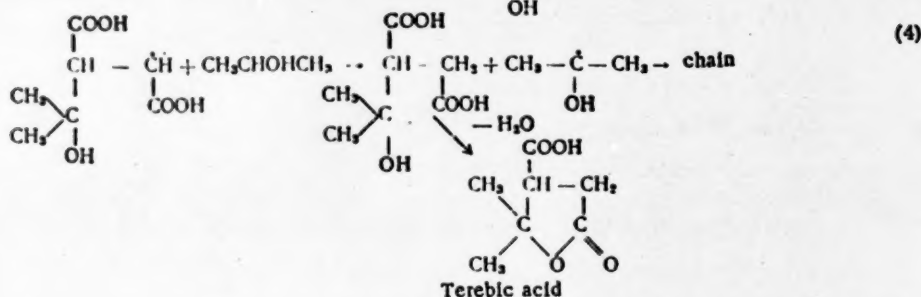
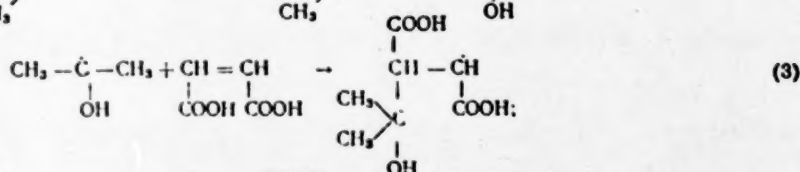
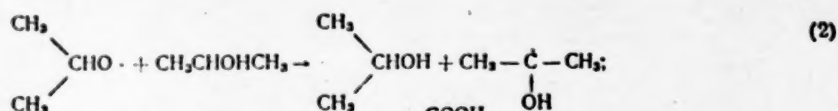
In one series of experiments, the reaction was carried out with the second carbon atom of the isopropanol labeled. In the other series of experiments, the reaction was carried out with inactive alcohol and diisopropyl peroxydicarbonate labeled in the second carbon atom. The activities given below are measurement data, calculated on the labeled second carbon atom. The radiometric measurements were made with an internal-filling counter. The measurement error was ± 3%. In the reaction of diisopropyl percarbonate (0.0016 mole) and maleic acid (0.0065 mole) with labeled isopropanol (0.19 mole; 39600 counts/min), the activity of the terebic acid (33779 counts/min) corresponded to 85.5% of the activity of the alcohol taken.

In the reaction of C¹⁴-labeled diisopropyl percarbonate (0.0013 mole; 39600 counts/min) with maleic acid (0.0064 mole) in inactive isopropanol (0.18 mole), the activity of the terebic acid (252 counts/min) was only 0.6%

of the activity of the peroxide taken. Hence we can conclude that the radicals $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} - \text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$ formed by decomposition of the percarbonate do not add to maleic acid and do not isomerize to $\text{CH}_3 - \overset{\cdot}{\text{C}} - \text{CH}_3$ radicals, as otherwise they would have been incorporated in the terebic acid. This conclusion agrees with data obtained previously on the mechanism of percarbonate decomposition in isopropanol [2]. The low activity found in the terebic acid is caused by the fact that labeled isopropanol accumulates in the system as the peroxide decomposes.

On the basis of the data obtained, the following scheme may be put forward for the reaction:





Acetone is formed as a result of chain termination through the radicals $\text{CH}_3-\overset{\cdot}{\text{C}}(\text{OH})\text{CH}_3$.

The 2,4-dinitrophenylhydrazone (333 counts/min) isolated after the reaction of maleic acid and C^{14} -labeled diisopropyl percarbonate (39600 counts/min) in inactive isopropanol contained only 0.8% of the activity of the starting peroxide.

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NEW METHOD OF PREPARING S-AMINOACYL DERIVATIVES OF CYSTEINE PEPTIDES

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(Presented by Academician M. M. Shemyakin, September 21, 1960)

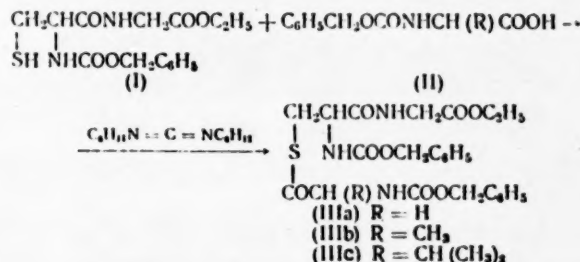
Translated from Doklady Akademii Nauk SSSR, Vol. 136, No. 6, pp. 1351-1353, February, 1961

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We showed previously [1] that the carbodilimide method of synthesizing peptides may be used successfully for the synthesis of O-aminoacyl derivatives of serine and tyrosine peptides, which are a class of compound that have recently been named depsi-peptides [2, 3]. In the present communication we give data on the use of N,N'-dicyclohexylcarbodiimide for the synthesis of S-aminoacyl derivatives of cysteine peptides, which it is convenient to regard as thiodepsi-peptides. The latter are of interest as the considerable lability of the S-CO bond of the mercaptoacyl group makes them capable of various rearrangements that may be of biochemical interest [4, 5].

Up to now, the main method of preparing certain thiodepsi-peptides has been the reversible transfer of aminoacyl residues from S-aminoacyl derivatives of thiophenol to compounds containing a free sulfhydryl group [4].* This method was used to obtain S-acyl, S-aminoacyl, and S-peptide derivatives of cysteamine [4], glutathione [4], and coenzyme A [10]. The fusion of cysteamine hydrochloride with amino acid chlorides has also been used for preparing S-aminoacyl derivatives of cysteamine [11]. In addition, the synthesis of an S-aminoacyl derivative of N-formylcysteine by the acid chloride method has been described in the literature [12].

In the method we propose, the mercaptoacyl group is formed by condensation of an ester of the cysteine-containing peptide (I) with carbobenzoxyamino acids (II) by means of N,N'-dicyclohexylcarbodiimide. This method was used to prepare esters of S-carbobenzoxycysteine-N-carbobenzoxycysteine (IIIa-IIIc).



Compounds (IIIa-IIIc) were synthesized under conditions analogous to those we described previously [1] for the preparation of O-aminoacyl derivatives of serine peptides (equimolecular amounts of reagents in the presence

* The starting S-aminoacyl derivatives of thiophenol were obtained by the reaction of hydrochlorides of amino acid chlorides with thiophenol [6] or by means of mixed anhydrides with the use of chlorocarbonic ester [7]. The latter was also used for the synthesis of a series of S-aminoacyl derivatives of thioglycolic, thiopropionic, and some other thio acids [8, 9].

of pyridine at room temperature). In all cases, the thiopeptides formed were isolated in a crystalline state in a high yield.

Thus, N,N'-dicyclohexylcarbodiimide makes it possible to synthesize compounds in which the amino acid residues are connected not only by an amide or ester bond, but also a thioester bond.

EXPERIMENTAL

1. Ethyl ester of N-carbobenzoxy-L-cysteinylglycine (I) (cf. [12]). A mixture of 5.7 g (0.008 mole) of the diethyl ester of dicarbobenzoxy-L-cystinylglycine [13, 14] in 125 ml of CH_3ON , 2.5 g of Zn dust, and 10 ml of 4 N sulfuric acid was boiled for 4 hr. The warm solution was filtered, the residue on the filter washed with methanol, and the filtrate evaporated in vacuum. The precipitated substance was collected and washed with water. We obtained (I) in quantitative yield and it had m. p. 118-120° (from aqueous ethanol) and $[\alpha]_D^{20} - 21.3^\circ$ (c = 2% in glacial acetic acid).

Found %: C 53.22; H 6.14; N 8.20. $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_5\text{S}$. Calculated %: C 52.92; H 5.91; N 8.23.

2. Preparation of S-aminoacyl derivatives of the ethyl ester of N-carbobenzoxy-L-cysteinylglycine. To a solution of equimolecular amounts of the ethyl ester of N-carbobenzoxy-L-cysteinylglycine (I) and the appropriate N-carbobenzoxyamino acid (II) in the minimal amount of acetone were added equimolecular amounts of pyridine and N,N'-dicyclohexylcarbodiimide, dissolved in the minimal amount of acetone. The reaction mixture was left at room temperature for 24 hr. The N,N'-dicyclohexylurea liberated was removed by filtration and washed with acetone. The filtrate was evaporated to dryness in vacuum and the residue recrystallized from an appropriate solvent.

Data on compounds (IIIa-IIIc) obtained by this method are given below.

Ethyl ester of S-carbobenzoxylglycyl-N-carbobenzoxy-L-cysteinylglycine (IIIa). The yield was 86% and the product had m. p. 120-122° (aqueous acetone) and $[\alpha]_D^{20} - 21.2^\circ$ (c = 2% in glacial acetic acid).

Found %: C 56.80; H 5.54; N 8.16. $\text{C}_{25}\text{H}_{33}\text{N}_3\text{O}_8\text{S}$. Calculated %: C 56.48; H 5.49; N 7.90.

Ethyl ester of S-carbobenzoxy-L-alanyl-N-carbobenzoxy-L-cysteinylglycine (IIIb). The yield was 68% and the product had m. p. 113-115° (CCl_4); $[\alpha]_D^{20} - 32.9^\circ$ (c = 2% in glacial acetic acid).

Found %: C 56.96; H 5.83; N 7.62. $\text{C}_{26}\text{H}_{31}\text{N}_3\text{O}_8\text{S}$. Calculated %: C 57.23; H 5.72; N 7.68.

Ethyl ester of S-carbobenzoxy-L-valyl-N-carbobenzoxy-L-cysteinylglycine (IIIc). The yield was 65% and the product had m. p. 105-106° (CCl_4); $[\alpha]_D^{20} - 41.0^\circ$ (c = 2% in glacial acetic acid).

Found %: C 58.70; H 6.27; N 7.35. $\text{C}_{28}\text{H}_{35}\text{N}_3\text{O}_8\text{S}$. Calculated %: C 58.62; H 6.15; N 7.32.

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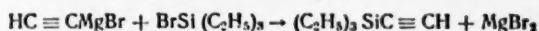
SYNTHESIS AND REACTIONS OF SILICOACETYLENES

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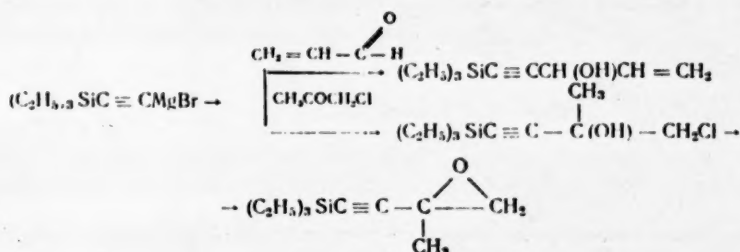
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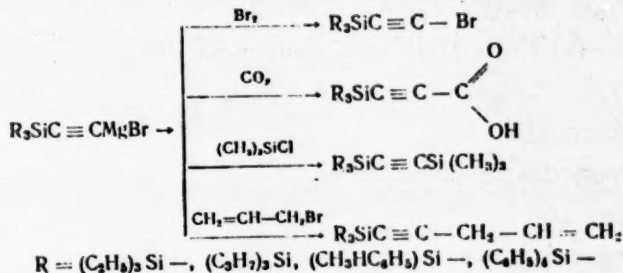
We previously established [1] that the reaction



proceeds in tetrahydrofuran to give a high yield (85%) of triethylsilylacetylene, which readily forms an organo-magnesium compound that is able to react with carbonyl compounds.



Continuing these investigations, in the present work we synthesized various silicoacetylenes and prepared some of their derivatives according to the following scheme:



In the vibrational spectra of monosubstituted silylacetylenes containing the triple bond in the position α to the silicon, attention is attracted by the low value of the frequency of the $C\equiv C$ vibration (about 2030 cm^{-1}), and this may be compared with the analogous reduction in the frequency of $C\equiv C$ vibrations in vinylsilanes [2]. This effect was expressed much less sharply in the spectra of disubstituted silylacetylenes [3].

In the infrared spectrum of $(C_2H_5)_3SiC\equiv C-COOH$, wide bands close to 2630 and 2508 cm^{-1} corresponded to the valence vibrations of the hydroxyl: The position of these bands, which characterize the strength of the hydrogen bonds, indicates that this acid is somewhat stronger than saturated aliphatic acids (but weaker than dibasic acids). A comparison of the dissociation constants of triethylsilyl ethynylcarboxylic and acetic acids confirmed this conclusion.

No.	Compound	B.p., °C	P, mm	n_D^{20}	d_4^{20}	MR _D		Yield, %
						found	calc.	
1	$(n-C_4H_9)_3SiC\equiv CH$	97-97.5	20	1.4376	0.7980	59.95	60.59	77
2	$CH_3(H)C_2H_4SiC\equiv CH$	92.5	42	1.5159	0.9169	48.17	48.59	59
3	$C_2H_5(H)C_2H_4SiC\equiv CH$	90	17	1.5161	0.9161	52.76	52.87	58.5
4	$(C_2H_5)_2Si(C\equiv CH)_2$	78-79	84	1.4393	0.8147	41.03	44.52	34
5	$(C_2H_5)_3SiC\equiv CH$	77.5-78.5	15	1.4429	0.8094	58.71	53.82	—
6	$(C_2H_5)_3SiC\equiv C-COOH$	132.2-132.8	3	1.4682	0.9339	84.29	53.30	50
7	$(n-C_4H_9)_3SiC\equiv C-Br$	115.5-116	11	1.4740	1.0688	68.73	68.68	80**
8	$CH_3(H)C_2H_4SiC\equiv C-CH_2-CH=CH_2$	120.5-120.7	13	1.5280	0.9258	61.97	62.17	64.5**
9	$CH_3(H)C_2H_4SiC\equiv C-Si(CH_3)_3$	129-129.5	27	1.5039	0.8968	72.12	72.27	58
10	$(CH_3)_2(H)C_2H_4SiC\equiv C$	166	6	1.5579	0.9810	87.30	87.22	—
11	$(C_2H_5)_2Si(C_2H_5)_2C\equiv C$	172-174	3	1.5598	0.9732	96.53	96.88	—
12	$(C_2H_5)_3SiC\equiv CH$ ***	m.p. 48.5-49	1.5	—	—	—	—	—

*MR_D calc was calculated from Vogel's values.

** Yield calculated on the silicohydrocarbon reacting.

*** In contrast to trialkylsilylacetylenes, this silicohydrocarbon is readily hydrolyzed by water, even in the cold, to form $(C_2H_5)_3SiOH$ with m. p. 152-164°.

In all the syntheses of monosubstituted silicoacetylenes, we obtained small amounts of the corresponding disubstituted acetylenes.

The table gives the properties of the alkyl- and alkylaryl, silylmonoacetylenes of the type $\geq Si-C\equiv CH$, some of their derivatives of the type $\geq Si-C\equiv C-\Phi$ (where $\Phi = Br, COOH$, etc.), disubstituted monoacetylenes of the type $\geq Si-C\equiv C-Si\leq$, and also dialkyldiethynylsilanes of the type $R_2Si-(C\equiv CH)_2$.

EXPERIMENTAL

Synthesis of tripropylsilylacetylene $(n-C_3H_7)_3SiC\equiv CH$ (1). Ethynylmagnesium bromide was prepared by Jones's method [4] from 10.0 g of magnesium, 50.0 g of ethyl bromide, and acetylene in 310 ml of dry tetrahydrofuran; 60.5 g of tripropylbromosilane was then added. The contents of the flask were stirred for 10 hr and decomposed with a saturated solution of NH_4Cl .

Found %: C 71.62; H 12.49; Si 15.65. $C_{11}H_{22}Si$. Calculated %: C 72.50; H 12.10; Si 15.40.

In the same way we prepared $(n-C_3H_7)_2Si(C\equiv CH)_2$ (5), $C_2H_5(H)C_6H_5SiC\equiv CH$ (3):

Found %: C 75.22; H 7.64; Si 17.20. $C_{10}H_{22}Si$. Calculated %: C 75.00; H 7.50; Si 17.50.

$CH_3(H)C_6H_5SiC\equiv CH$ (2):

Found %: Si 18.7. $C_9H_{10}Si$. Calculated %: Si 19.1.

$(C_2H_5)_2Si(C\equiv CH)_2$ (4):

Found %: C 70.40; H 8.96; Si 20.32. $C_8H_{12}Si$. Calculated %: C 70.40; H 8.88; Si 20.16.

$(C_2H_5)_3SiC\equiv CH$ (12):

Found %: Si 10.0. $C_{20}H_{46}Si$. Calculated %: Si 9.9.

Synthesis of $(C_3H_7)_3SiC \equiv CBr$. To tripropylsilylethynylmagnesium bromide (from 2.4 g of magnesium, 12.0 g of ethyl bromide, and 18.5 g of 1) in absolute ether was slowly added 8.0 g of dry bromine dropwise with stirring and cooling with CO_2 . A precipitate of $MgBr_2$ formed as the bromine was added. The contents of the flask were then hydrolyzed with dilute HCl , washed with saturated Na_2CO_3 solution and water, and dried. The ether was removed and the residue vacuum distilled. We isolated (7).

Found %: Br 30.17. $C_{11}H_{21}SiBr$. Calculated %: Br 30.56.

Synthesis of $(C_2H_5)_3SiC \equiv C-COOH$ (6).* From 2.9 g of magnesium, 14.0 g of ethyl bromide, and 17.0 g of $(C_2H_5)_3SiC \equiv CH$ in absolute ether we prepared triethylsilylethynylmagnesium bromide, which was then poured onto 0.5 kg of crushed CO_2 . After the normal treatment, distillation yielded 11.0 g of (6). The neutralization equivalent, found by titration with 0.1 N $NaOH$, was 187.8; the neutralization equivalent equal to the molecular weight was 184.3.

Infrared spectrum ν (cm^{-1}): 735 (v.s. dbl.), 797 (v.s.), 965, 968 (v.w.), 977 (av.), 1013 (s. dbl.), 1070 (w.), 1157 (w.), 1246 (v.w.), 1265 (v.s.), 1355 (v.w.), 1378 (w.), 1390 (av.), 1412 (s.), 1468 (av.), 1695 (v.s., at edges of unresolved maxima at 1665 and 1695 cm^{-1}) 2180 (av.), 2508 (av.), 2630 (av.), 2765 (v.w.), 2820 (av.), 2898 (v.s.), 2920 (v.s.), 2975 (v.s.), 3100 (av., on background at 2975).

The bands at 2630, 2508, 1695 and 1265 cm^{-1} were connected with vibrations of the group $\begin{array}{c} O \\ \parallel \\ C \\ | \\ OH \end{array}$, the band at 2180 cm^{-1} corresponded to vibrations of the $C \equiv C$ bond, and the very strong bands at 1246 and 797 cm^{-1} indicated the presence of a $Si(C_2H_5)_3$ group. We also prepared the silver salt of the acid, which exploded violently in the dry state.

Found %: C 58.66; H 9.25; Si 15.25. $C_9H_{16}SiO_2$. Calculated %: C 58.66; H 8.75; Si 15.24.

Synthesis of $C_7H_9(H)C_6H_5SiC \equiv C-CH_2-CH=CH_2$ (8). To the organomagnesium compound prepared from 2.0 g of magnesium, 12.0 g of ethyl bromide, and 11.02 g of (2) was added 11.0 g of allyl bromide. The contents of the flask were boiled for 5 hr in ether, the ether removed, and the residue heated for an hour on a water bath. The complex was decomposed and then treated in the usual way.

Infrared spectrum ν (cm^{-1}): 731 (s.), 748 (s.), 837 (v.s.), 882 (v.s.), 916 (s.), 928 (av.), 991 (s.), 998 (s.), 1034 (s.), 1087 (w.), 1117 (v.s.), 1186 (w.), 1253 (av.), 1282 (w.), 1315 (w.), 1420 (av.), 1430 (av.), 1650 (av.), 2170 (s.), 2200 (s.), 2817 (w.), 2854 (v.w.), 2891 (w.), 2918 (w.), 2970 (av.), 3021 (av.), 3057 (av.), 3074 (av.), 3096 (av.). The bands at 2200 and 2170 cm^{-1} were evidently connected with valence vibrations of $C \equiv C$ and $Si-H$ (δ_{SiH} 916 cm^{-1}). The absorption at 3096 and 1650 cm^{-1} indicated the presence of a $C=CH_2$ group.

$CH_3(H)C_6H_5SiC \equiv C-Si(CH_3)_3$ (9) was prepared analogously.

The infrared spectra were plotted and interpreted by A. N. Lazarev, to whom we are very grateful.

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* By passing CO_2 into triethylsilylethynylmagnesium bromide, we obtained crystals, which decomposed during distillation and determination of the melting point. We preliminarily assigned the formula of the acid to these crystals [1].

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CATALYTIC CONVERSIONS OF N,N-DIALKYLCYCLOHEXYLAMINES

R. D. Ėrlikh, S. V. Dobrovol'skii, and A. I. Korolev

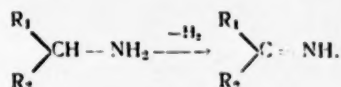
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Literature data on vapor-phase catalytic dehydrogenation of amines are limited to the work of A. A. Balandin et al. [1, 2] on the dehydrogenation of primary aliphatic amines on metal catalysts. According to this work, amines lose a molecule of hydrogen on dehydrogenation to form a C=N bond:



As the scheme shows, the conversion of amines to ketimines may be effected only in the case of primary or secondary amines. It seemed very interesting to study the dehydrogenation of tertiary amines, which apparently cannot form ketimines. In the present communication we give the results of investigating the catalytic dehydrogenation of tertiary amines on the example of N,N-dimethyl- and N,N-diethylcyclohexylamine.

The reaction was carried out at atmospheric pressure in a flow system in the temperature range of 220-300°. The catalyst, which was 20% CuAl₂O₃, was prepared by impregnating Al₂O₃ with copper nitrate solution with subsequent firing at 360° and reduction with hydrogen at 250°. In the first part of the work we studied N,N-dimethylcyclohexylamine with b. p. 158-159°, n_D²⁰ 1.4530. Literature data [3]: b. p. 158-159°, n_D²⁰ 1.4528.

The catalytic reaction yielded a liquid catalyzate and a gas, which consisted of pure hydrogen. Acid hydrolysis of the catalyzate led to the isolation of the "ketonic part," and according to analysis this consisted of cyclohexanone and 2-methylcyclohexanone. The latter was identified as the 2,4-dinitrophenylhydrazone, which formed orange leaflets (from alcohol) with m. p. 135°. Literature data [4]: m. p. 135°.

Found %: N 19.19, 19.05. C₁₃H₁₉N₄O₄. Calculated %: N 19.16.

In a search for conditions producing an increase in the yield of ketones, we tried dilution of the starting amine with hydrogen, nitrogen, and water vapor. The best results were obtained with water vapor, and in this case 85-90% of the N,N-dimethylcyclohexylamine taken was converted into ketones.

For separate determination of the cyclohexanone and 2-methylcyclohexanone in the mixture we used a simplified procedure based on the low solubility of 2-methylcyclohexanone semicarbazone in 40% alcohol, which we observed. By this procedure, the total content of ketones in the "ketonic part" isolated in the experiment was determined by oxime formation and then the amount of 2-methylcyclohexanone determined on a separate sample with the cyclohexanone content finally calculated by difference. In a series of experiments we studied the relation of the yield of ketones, calculated on the amine passed, to the temperature and degree of dilution with water vapor. In all experiments the load of N,N-dimethylcyclohexylamine on the catalyst was constant and equalled 100 g/liter·hr. The results of these experiments are given in Figs. 1 and 2.

In several experiments we isolated the mixture of amines remaining in the acid hydrolyzate after distillation of the "ketonic part." As analysis showed, the mixture consisted of unconverted *N,N*-dimethylcyclohexylamine, dimethylamine, and methylamine.

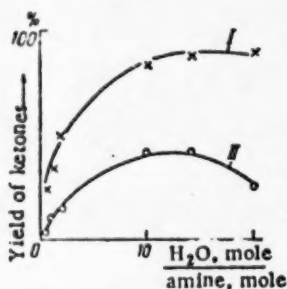


Fig. 1. Relation of yield of ketones to the degree of dilution with water vapor at 280°: I) mixture of ketones; II) 2-methylcyclohexanone.

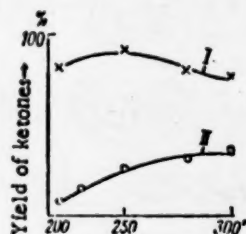
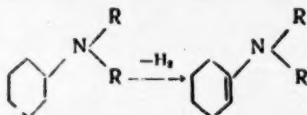


Fig. 2. Relation of yield of ketones to temperature. Molar ratio of amine: water 1: 10. I) Mixture of ketones; II) 2-methylcyclohexanone.

The study of the catalytic conversion was continued with *N,N*-diethylcyclohexylamine, which was obtained by the method in [5] and had b. p. 193–194°. Literature data [5]: b. p. 193°. At 280°, a space velocity of 0.1 hr⁻¹, and a molar ratio of amine: water of 1: 10, we obtained a mixture of ketones containing approximately 30% of 2-ethylcyclohexanone and 70% of cyclohexanone. The 2,4-dinitrophenylhydrazone of 2-ethylcyclohexanone formed bright red needles (from alcohol) with m. p. 161°. Literature data [6]: m. p. 162°.

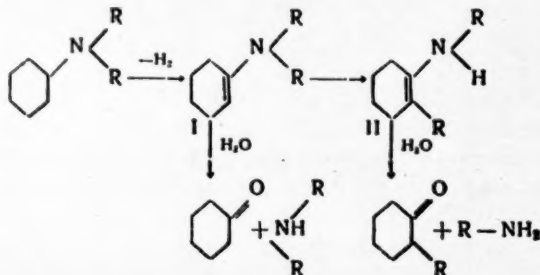
Found %: N 18.28, 18.48. C₁₄H₁₈N₄O₄. Calculated %: N 18.30.

Thus, the results of the present investigation show that on a Cu–Al₂O₃ catalyst in the presence of water vapor, *N,N*-dialkylcyclohexylamines undergo catalytic conversion to a mixture of two ketones, namely cyclohexanone and 2-alkylcyclohexanone. It may be surmised that the first stage of the conversion is dehydrogenation of the cyclohexane nucleus to form an α, β -unsaturated amine:



According to literature data [7, 8], α, β -unsaturated amines, which are better known as enamines, have a clearly expressed tendency to undergo electrophilic substitution at the β -C atoms. In addition, enamines are readily hydrolyzed by water to form carbonyl compounds [9].

In view of these properties of enamines, the catalytic conversion we discovered is explained in the following way: The enamine (I) initially formed rearranges to a β -alkylenamine (II), which is then hydrolyzed to form a 2-alkylcyclohexanone; the cyclohexanone always present in the mixture is formed by hydrolysis of the enamine (I):



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SYNTHESIS OF UNSATURATED ORGANOSILICON PEROXIDES

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(Presented by Academician B. A. Arbuzov, September 28, 1960)

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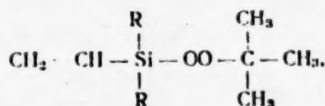
Original article submitted September 24, 1960

In addition to organic peroxides, organosilicon peroxides of various types have recently attracted the attention of chemists. The preparation of organosilicon peroxides of the types $(R)_3Si-OO-Si(R)_3$ (I) and $(R)_3SiOOH$ (II) was first mentioned in Berry's patent [1]. Buncel and Davies [2, 3] later gave a detailed characterization of a series of mixed peroxides of the type $(R)_3Si-OO-C(R)_3$ (III). Hahn and Metzinger [4] described the preparation and characteristics of these types of compound; the first two were synthesized mainly by the reaction of trialkyl- and triarylmonochlorosilanes with hydrogen peroxide or sodium peroxide and the third type, by the reaction with alkyl hydroperoxides. Original methods were also used. Thus, in patent [1] it is recommended that the first type of peroxide be prepared by the reaction of sodium monosilanolates with chlorine or bromine, and in the work of Pike and Schaffer [5], from tetraalkylsilanes through the sulfates with subsequent reaction of the sulfates with hydrogen peroxide. The same authors prepared the third, mixed type by the reaction of trialkylsilylamines with alkyl hydroperoxides.

Judging by literature data, organosilicon peroxides differ from organic peroxides in a number of characteristics, namely lower thermal stability [3, 4], a tendency to rearrange, as demonstrated in the work of Buncel and Davies [6], and also the nature of the infrared spectra [7].

The authors of [3, 4] recommend these compounds for polymerization initiation and also as oxidants.

A review of the literature shows that unsaturated organosilicon peroxides have not been synthesized or investigated yet; it should be noted that unsaturated organic peroxides have been studied little as yet. We undertook the synthesis of a series of vinyl organosilicon peroxides of the third, mixed type with the general formula:



with one, two, and three peroxide groups.

Preparation of mono-tert-butylperoxymethylvinylethylsilane $CH_2 = CH-Si(CH_3)(C_2H_5)OOC(CH_3)_3$. The starting methylvinylethylchlorosilane was synthesized by the reaction of methylvinylchlorosilane with ethylmagnesium bromide with subsequent characterization by the chlorine content, which was found to equal 26.2% (theoretical 26.4%).

The peroxide was synthesized in the following way. A mixture of 18 g of tert-butyl hydroperoxide (100%) and 15.8 g of pyridine in 50 ml of ligroin was added dropwise with vigorous stirring to a solution of 27 g of freshly distilled methylvinylethylchlorosilane in 150 ml of ligroin (b. p. up to 35°) at -3°. The reaction proceeded vigorously, but the temperature of the reaction medium was kept below 0°. After the addition, when the

mixture had been kept at room temperature for 3 hr, the precipitate of pyridine hydrochloride was removed with water and the organic layer washed with water and dried over magnesium sulfate. After removal of the ether, the peroxide was distilled at 4 mm Hg and 31°. We obtained a total of 22 g of peroxide. The peroxide obtained was a clear liquid with the following characteristics: n_D^{20} 1.4206, d_4^{20} 0.8565; σ_{20} 24.22 dyne/cm; molecular weight (cryoscopically in C_6H_6) 179, calc. 188.32; MR 55.74, calc. 55.96.

Found %: C 57.28; H 10.88; Si 14.83. $C_9H_{20}SiO_2$. Calculated %: C 57.40; H 10.70; Si 14.90.

The active oxygen was determined iodometrically: found 8.4%, calculated 8.49%. Decomp. p. 173°.

The structure of the peroxide formed was confirmed by reduction: 5.8 g of peroxide was shaken for 6 hr at room temperature with 6 g of anhydrous sodium sulfite in 40 ml of water. After standing for 30 min, the upper layer was separated, dried, and distilled at atmospheric pressure. We obtained three fractions with b. p. 75-82° ($n = 1.388$); 82-120° ($n = 1.395$) and 120-145° ($n = 1.429$). Redistillation of the latter yielded a fraction with b. p. 134-136° (n_D^{20} 1.4321), which we considered to be methylvinylethylsilanol. Distillation of the aqueous layer also yielded tert-butanol.

Preparation of di-tert-butylperoxymethylvinylsilane $CH_2=CH-Si(CH_3)(-OO-C(CH_3)_3)_2$. By the method described, from 21.2 g of freshly distilled methylvinylchlorosilane ($d = 1.09$, chlorine 50.3%, theoretical 50.2%) and 27 g of tert-butyl hydroperoxide in the presence of 23.8 g of pyridine we obtained 18.8 g of peroxide with b. p. 90-91° (20 mm Hg), 79° (11 mm), and 41-42° (1 mm). The peroxide was a liquid with the following characteristics: n_D^{20} 1.4210, d_4^{20} 0.9206; σ 24.83 dyne/cm; molecular weight 243.5, calc. 248.37; MR 68.42, calc. 68.27.

Found %: C 53.13; H 9.89; Si 11.41. $C_{11}H_{24}SiO_4$. Calculated %: C 53.19; H 9.74; Si 11.30.

Active oxygen found 12.64%; calculated 12.88%. Decomp. p. 105.5° (with explosion).

Preparation of di-tert-butylperoxyvinylethylsilane $CH_2=CH-Si-(C_2H_5)(-OO-C(CH_3)_3)_2$. We synthesized the starting vinyl ethyldichlorosilane by the action of ethylmagnesium bromide on vinyltrichlorosilane in absolute ether. Isolation and distillation yielded vinyl ethyldichlorosilane with b. p. 123° and a chlorine content of 45.9% (theoretical 45.7%).

By the method described above, from 23.3 g of vinyl ethyldichlorosilane and 27 g of tert-butyl hydroperoxide in the presence of 23.8 g of pyridine we obtained a peroxide, which distilled at 63° (2 mm). The peroxide obtained was a clear liquid with the following characteristics: n_D^{20} 1.4241, d_4^{20} 0.9112; σ_{20} 25.75 dyne/cm; molecular weight 256, calculated 262.4.

Found %: C 54.75; H 9.88; Si 11.06. $C_{12}H_{26}SiO_4$. Calculated %: C 54.93; H 9.99; Si 10.69.

MR 73.49; calc. 72.92; active oxygen content found 12.3%, calculated 12.19%. Decomp. p. 159° (with explosion).

Preparation of tri-tert-butylperoxyvinylsilane $CH_2=CH-Si(-OO-C(CH_3)_3)_3$. By this method, from 16.2 g of freshly distilled vinyltrichlorosilane ($d = 1.27$, chlorine 65.8%) and 27 g of tert-butyl hydroperoxide in the presence of 23.8 g of pyridine we obtained a peroxide, which distilled (in vacuum with nitrogen passed through a capillary) within the range of 75-80° (1 mm). In redistillation at the same residual pressure, we collected 13 g of a fraction with b. p. 78°. The peroxide obtained was a clear liquid with the following characteristics: n_D^{20} 1.4237, d_4^{20} 0.9576; σ_{20} 25.96 dyne/cm; molecular weight 317, calc. 322.57; MR 85.83, calc. 85.22.

Found %: C 52.03; H 9.14; Si 8.68. $C_{14}H_{30}SiO_6$. Calculated %: C 52.15; H 9.38; Si 8.70.

Active oxygen found 14.2%, calculated 14.89%. Decomp. p. 147.5° (with explosion).

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